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JOURNAL OF CHEMICAL EDUCATION

for July, 1938

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Volume 15, Number 7 Contains

FRONTISPIECE—PETER DEBYE 301

EDITOR'S OUTLOOK 302

1938: THE ONE HUNDREDTH ANNIVERSARY OF THE BIRTH OF FRIEDRICH KONRAD BEILSTEIN 303
Ernest H. Huntress

HOW BEILSTEIN IS MADE 310
Friedrich Richter

COLLATERAL READINGS IN INORGANIC CHEMISTRY 317
L. A. Goldblatt

AN EXPERIMENT ILLUSTRATING THE RELATION BETWEEN E.M.F. AND THE EQUILIBRIUM CONSTANT 320
Robert Livingston and J. J. Lingane

THE TEACHING OF QUALITATIVE ANALYSIS BY THE SEMIMICRO METHOD 324
Grant W. Smith

METHODS FOR THE GRAPHICAL REPRESENTATION OF QUATERNARY SYSTEMS INVOLVING RECIPROCAL SALT PAIRS, MAKING POSSIBLE THE EXTRAPOLATION OF TIE-LINES 329
John E. Ricci and Charles M. Loucks

CORRESPONDENCE:

PYRENE 333

CHEMICAL EQUATIONS. *Ralph E. Silker* 334

"PREPARATION OF CONSTANT-BOILING HYDROBROMIC ACID." *Ernest M. Marshall* 334

AN INEXPENSIVE BURET HOLDER 335
Olus J. Stewart

ISOTOPES AND ANALYTICAL STANDARDS—A CORRECTION 335

CHANGING CONCEPTION OF TEACHING HELPS IN COLLEGE GENERAL CHEMISTRY TEXTBOOKS 336
Ralph E. Dunbar

A STATISTICAL EVALUATION OF STUDENT GRADES IN QUANTITATIVE ANALYSIS 339
Rev. Francis W. Power, S.J.

WHY SOLVE FOR X? 342
Ewing C. Scott

THE CONSTRUCTION OF AN INEXPENSIVE CONSTANT TEMPERATURE WATER BATH FOR SOLUBILITY MEASUREMENTS 343
William Jacob Knox, Jr.

A RAPID SOLUTION DISPENSING PIPET 344
B. J. Otte, P. J. Thompson, and G. A. Barber

ABSTRACTS 345

RECENT BOOKS 347

TRADE ANNOUNCEMENTS VIII

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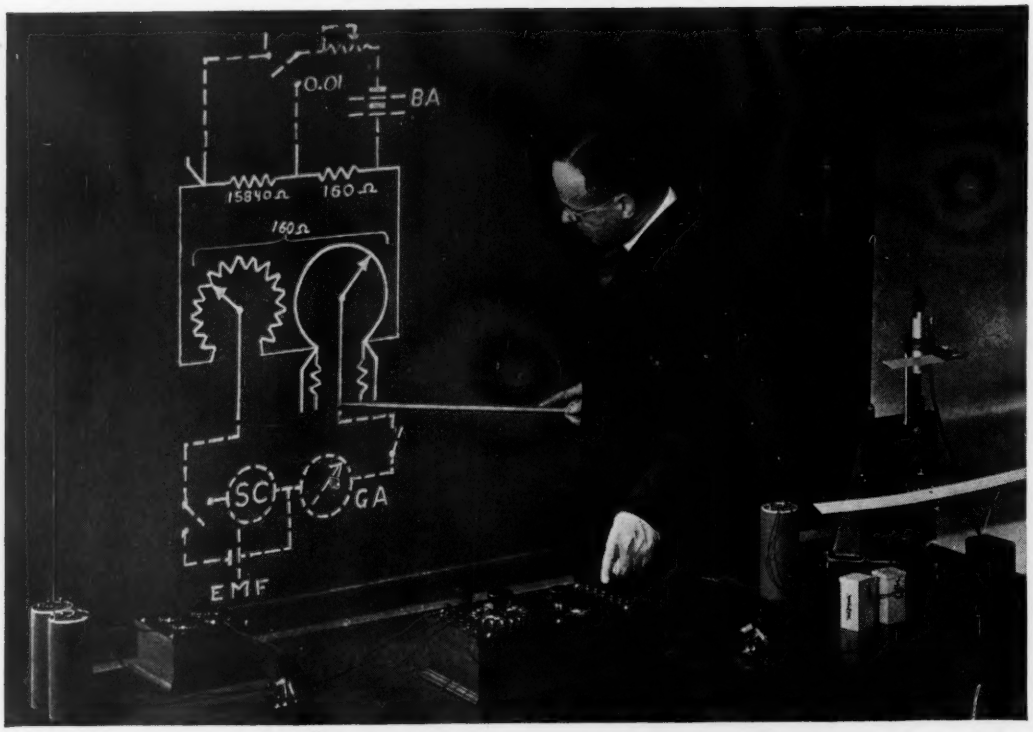

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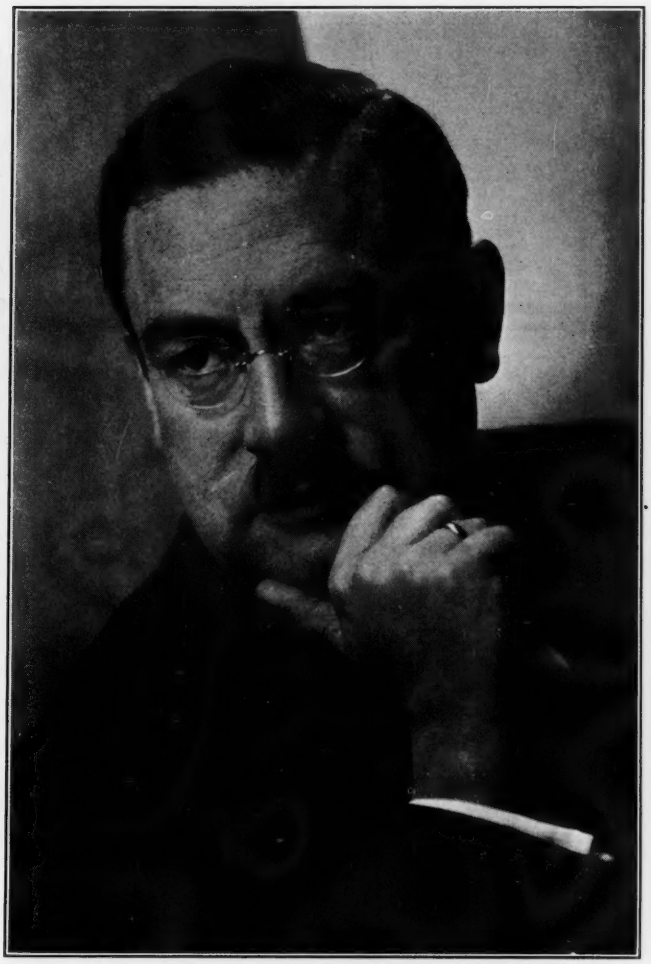

PETER DEBYE (1884–)

Chemistry and physics are now so closely knit together that no unnatural comment was raised when the 1936 Nobel Prize in Chemistry was awarded to a physicist for his studies of the structure of molecules as revealed by dipole measurements and X-ray interference.

Peter Debye, born March 24, 1884, at Maastricht, Holland, was trained at Aachen (Dipl. ing. 1905), and Munich (Ph.D. 1908). His mature teaching career has included chairs in theoretical physics and direction of the laboratories at Zürich (1910), Utrecht (1912), Göttingen (1914), Technical High School, Zürich (1920), Leipzig (1927), Berlin (1935). Since 1935 he has also been Director of the Kaiser Wilhelm Institut für Physik at Berlin–Dahlem.

The principal goal of Professor Debye's work, both theoretical and experimental, has been to gain a more accurate insight into the molecular and atomic structure of matter in order to arrive at a clearer understanding of the behavior of materials. The chemists have benefited particularly from some of his many fields of research. His studies of X-ray diffraction led to the "powder" method of investigating materials and to the discovery of interference in liquids and eventually by single molecules. He has developed the use of dielectric and interferential procedures for determining structure. He has studied the resolution of spectral lines by refraction in liquids. He discovered a magnetic method of producing very low temperatures and has studied the T^3 law of specific heats at low temperatures. To him we owe the introduction of electrical dipoles to explain dielectric phenomena and the elucidation of anomalous dispersion and absorption in the field of electrical waves (high frequency losses). Most chemists know his name coupled with that of Erich Hückel; they have presented an extremely useful fundamental picture of an electrolytic solution.

Professor Debye has been awarded honorary doctorates by Brussels, Liége, Oxford, Harvard; he is a member of numerous academies and learned societies in Germany, Holland, Sweden, Denmark, U. S. S. R., Vatican City, Switzerland, England, and the United States (National Academy of Sciences, American Philosophical Society). His medals are: Rumford (1930); Faraday (1932); Lorentz (1935); Franklin (1937).

(Contributed by Ralph E. Oesper, University of Cincinnati)

EDITOR'S OUTLOOK

WHO'S A PESSIMIST? My great-uncle remembers a gag about a youth who spoke of a friend's pessimism, and by way of instance cited the gloomy conviction that all women are bad. A cynical elder, overhearing, snorted, "That boy's no pessimist—he's an optimist."

We feel somewhat the same way about people who believe that the country is going to hell in a handbasket because so many of the old principles have broken down, and so many of the ancient virtues are virtues no longer. We'd be less inclined to agree with their forecast of the country's destination if we could see eye to eye with them on the subject of the supposed causes.

If it is really true that our wise men now know how to lift themselves (and us) by their own bootstraps—if it is really true that the more we spend today the more we'll have tomorrow—if it is really true that we can support our aged on the interest from what we owe—if it is really true that one can reduce the retail price of overalls by raising the costs of cotton labor, and taxes—if it is really true that we can strengthen credit by defaulting debts—if it is really true that one can strengthen a rickety structure by encouraging termites to multiply in it—then we foresee for this country (and many others) the brightest kind of future.

Our so-called leaders unanimously proclaim these new "truths" daily, and they contrive by one means and another to give so many would-be nurselings a swig at the public teat that they seem in a fair way to convert a permanent majority to their way of thinking (or talking, at any rate).

Somehow we have difficulty in reassuring ourself that there can't possibly be any live powder left in any of the dud virtues and principles that they have so nonchalantly tossed into the incinerator. One of the unpopular things about virtues and principles has been that they seldom pay bonanza dividends directly and automatically. One of the nasty things about them is that it so often proves disastrous to discard them.

We'd feel more optimistic if we were altogether sure that all the rules of the game have really been changed. Something keeps suggesting to us that we have merely hired a slick coaching staff that's about due to collide with a hard-boiled referee.

1938: *The* ONE HUNDREDTH ANNIVERSARY *of the* BIRTH *of* FRIEDRICH KONRAD BEILSTEIN (1838–1906)*,†

ERNEST H. HUNTRESS

Massachusetts Institute of Technology, Cambridge, Massachusetts

THE year 1938 marks the one hundredth anniversary of the birth of an unusually large number of men who laid the foundations of modern organic chemistry. The list of illustrious names includes those of von Martius (January 19), E. W. Morley (January 29), Sir W. H. Perkin, Sr. (March 12) A. Crum-Brown (March 26), I. Stroof (April 8), L. de Boisbaudran (April 18), E. Lippmann (September 24), F. F. Lippich (October 4), B. Radziszewski (November 6), and W. W. Markownikow (December 22). To review the outstanding contributions to science of each member of this distinguished group would be both interesting and instructive, but quite impracticable within the time at our disposal. Upon this occasion, however, it is particularly appropriate to contemplate briefly the service to chemistry of another member of this centenary club whose one hundredth birthday anniversary on Thursday, February 17, 1938, is of special interest to organic chemists, *i. e.*, Friedrich Konrad Beilstein.[1]

Born of German parents in what was then St. Petersburg, his early education was completed in the excellent German schools of the Russian capital. At the tender age of fifteen he began the series of steps of his higher education which, only two days before his twentieth birthday in February, 1858, culminated in his doctor's degree. During this relatively short period he also traveled widely and studied with many of the masters. The first two years (1853–55) he spent at Heidelberg where his initial interest in chemistry was further inspired and directed by Bunsen. In 1855 he transferred to Munich where besides listening to the lectures of Liebig he pursued additional work in mathematics and physics, and under Jolly's supervision completed his first published experimental investigation entitled "Concerning the Diffusion of Liquids."[2]

In March, 1856, he returned to Heidelberg where for just another year he found himself associated with many contemporaries who also were to rise to eminence, such as Roscoe, Lothar Meyer, Landolt, Lieben, Quincke, von Baeyer, and particularly Hübner and Kekulé whose close intimates he became. March, 1857, found him at Göttingen where under Wöhler he established murexide as the ammonium salt of purpuric acid,[3] and obtained his doctor's degree.

A second period of migration was to ensue, however, before the real beginning of his main life work. Unable to find an appointment at Göttingen he spent an entire year at the École de Médecine in Paris with Würtz, during which he established a new friendship with his own contemporary, Friedel. Having determined to become a university teacher he then accepted an offer from Breslau as assistant to Löwig but had barely become established there when he was invited by Wöhler to return to Göttingen to take charge of a division. Gladly accepting this offer, he remained at Göttingen for six years (1860–66) actively engaged in organic research and closely associated with both Fittig and Hübner in editing the *Zeitschrift für Chemie*.

Through the courtesy of Dr. Friedrich Richter (present editor of the Beilstein *Handbuch*) and that of the Kekulé Archive at Darmstadt (Professor Fuchs, administrator) we print here a translation of a hitherto unpublished letter written by Beilstein to his friend Kekulé during this six-year stay at Göttingen.[4]

The letter follows:

Göttingen, June 3, 1860

Dear Herr Professor:

You are probably surprised: 1. to receive a letter from me at all, 2. to find me in Göttingen unless in some way the news of my change has already become known to you. You probably wonder what the purpose of my letter is—I am enough of an egoist to begin nothing without some object. However, I am not coming to the point at once; I first make fine phrases in order to make you gently disposed. I am very sorry that I did not meet you in Ghent; I could read only Kundig's musical farewell still on the blackboard—even Baeyer had disappeared without a trace—I saw only your servant who seemed in a very rosy mood and felt very much flattered to be visited by the acquaintance of his master. "Oh what a fine fellow, Mr. Kundig," he murmured steadily.

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* Contribution No. 169 from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology.

† Based on a dinner talk before members of the Northeastern Section of the American Chemical Society, February 11, 1938.

[1] For more complete biographical accounts compare those by HJELT, *Ber.*, **40**, 5041–78 (1907); by O. WITT, *J. Chem. Soc.*, **99**, 1646–9 (1911); by O. LUTZ, *Z. angew. Chem.*, **19**, 2058–60 (1906); and F. RICHTER, *Ber.*, **71A**, 33–55 (Feb., 1938); *Angew. Chem.*, **51**, 101–7 (Feb. 19, 1938).

[2] *Ann.*, **99**, 165–97 (1856).

[3] *Ibid.*, **107**, 176–91 (1858).

[4] A photograph of Beilstein kindly supplied by Professor Ernst Berl from the Kekulé album appeared in THIS JOURNAL, **15**, 51 (Feb., 1938).

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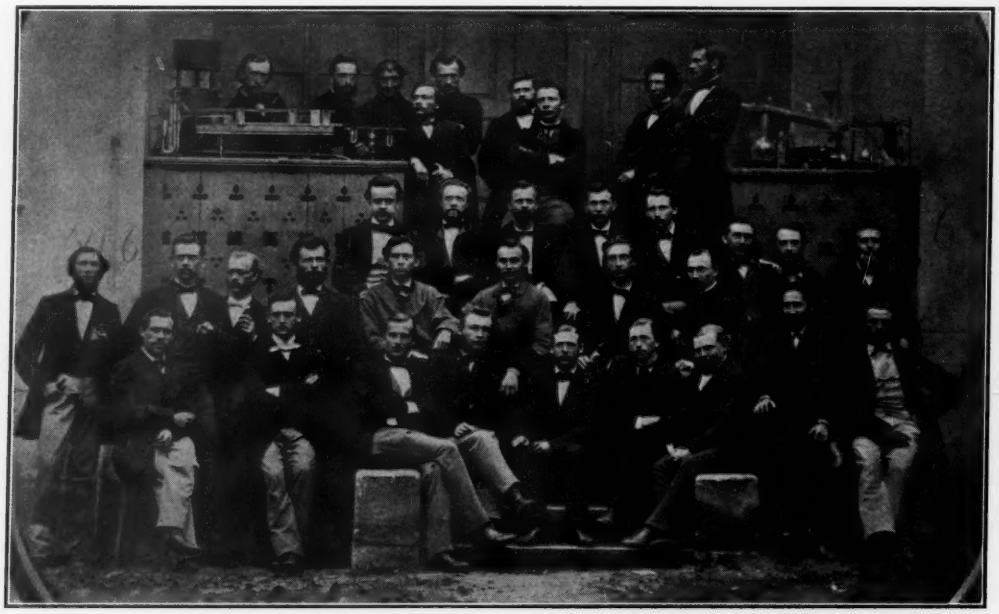


THIS PHOTOGRAPH WAS TAKEN IN GÖTTINGEN IN 1863 AND IS REPRODUCED HERE THROUGH THE COURTESY OF DR. F. RICHTER AND THAT OF FRL. DR. HÜBNER, DAUGHTER OF BEILSTEIN'S COLLABORATOR. THE PERSONS REPRESENTED ARE FROM LEFT TO RIGHT: FRONT ROW: ARONSTEIN, WEHRHASSE, REMIEN, APPEL, HELLMICH, WOLFF, BRÜTT, MEIER, WOLTERS. SECOND ROW: LOHMANN, BIRNBAUM, SALM, MICHAELIS, KUNZE, NEIMKE, HAUERS, BÖTTGER, BECKER, KLOSTERMANN, BERLIEW. THIRD ROW: WILHELMI, POPP, LEHMANN, BALLIN, STRÜVER. FOURTH ROW: ALEXEYEFF, HÜBNER, HAMPE, WILBRAND, KAISER, VON USLAR, KÜHNER, WÖHLER, BEILSTEIN

Finally I came to Breslau where I presented myself to my new patron (Löwig) and was very well received by him. I lived in the laboratory and had a very agreeable job: I never went into the laboratory before ten o'clock and was all through about twelve, in the afternoon coffee was drunk in genial fashion and from three until five there was work again, then I stayed on the job and "laboratized" as long as I chose. You see it was downright pleasant life. Löwig has his place in the third story and comes down only for one or one and a half hours in the afternoons; during the rest of the time my colleague and I are the lords of creation.

What shall I tell you about Löwig? In the city he is called "König" (king)—we called him only "Pascha." Woe to him who dared to work one whit differently from what he had been told. He is a chemist of the oldest school and since, fortunately, he had lost his book of lectures he was forced to work out a new one, *i. e.*, he copied (in part literally) the new and not at all bad book by Gorup—consequently he also has become a believer in types. The laboratory is fine, eighty-six fellows, three-fourths of whom are taking the pharmacist's examination, are working in it. Pascha behaves most graciously toward me and affords me all possible protection and facilities. Lothar Meyer is not getting on very well and he regrets having settled in Breslau. Allured by Landolt's whole lecture program he settled there and lectured on volumetric methods of analysis, physical chemistry, physiological chemistry, and so forth. He had trouble, however, to get through it all and he has even announced a review course for this summer. But it's no wonder; the only ones in Breslau are those taking pharmacists' examinations and miners and everything which is not necessary for the examination these people regard as superfluous. How is a young chemist to get along? Meyer is an assistant with Heidenhain in the physiological institute and has his own little laboratory there. That is all. Löwig will not countenance the combination of laboratory assistant and privat-dozent. When Landolt established himself as a lecturer he had to get out of the laboratory.

I had scarcely advised Wöhler of my happy landing in Breslau than he immediately telegraphed back asking whether I would not come to Göttingen in Geuther's place: naturally I had nothing more urgent to do than to accept—the only difficulty was informing Pascha. I finally took heart and told him of my decision to leave. . . strange to say, he was quite calm, although I found it advisable to ascribe a motive by the remark that at Göttingen I intended to become a tutor. This clarified matters for Pascha, and we parted friends. Apart from the chemical situation Breslau is a very pleasant place and now seems to me like a real paradise. When the time came I packed my things and came here. On the way I could not fail to look up Heintz who has made some interesting discoveries recently. Do you know him? He is a student of Rose's and a former apothecary —that tells everything. He is a most absolute empiricist and his, or rather Wislicenus' (privat-dozent in Zurich) formulas are nothing but misunderstood condensed types (see Couper). Having arrived here I made my official calls and was able to see Limpricht: he has agreed to go to Greisswald at 1600 German dollars and has already received 36,000 for the construction of a laboratory. That is an unheard of thing in Prussia since neither Bonn nor Berlin has laboratories and in Halle chemistry exists in a room in a private house—apropos Berlin—do you know who is headed for Berlin? No less than my former master Pascha Löwig—he is pushing the fat Mitscherlich fabulously and has already presented plans for the laboratories to the Ministry of Education. On the other hand, Frerichs, whose influence in Berlin is very important, will work very hard in appointing Staedler. "Chancel is a fool," Würtz once said at the École de Médicin. "But how could Gerhardt attach himself to a man without talent?" we asked. "Because he polished his boots," Würtz told us.

"The Limpricht Division" is now represented by the chief assistants, Geuther and von Uslar. They have not wanted to make either one of these simpletons professors. That they have no attractive power readily follows from the fact that during Limpricht's time this division consisted of fifty to sixty men, now there are only thirty in it—six of his favored and faithful ones followed Limpricht to his new place.

In the new establishment work is going on actively. The old shed forms the left wing; on the right side of the middle building stands a similar wing; to each of these wings another one hundred-foot wing joins perpendicularly and the front is two hundred seven feet long. You see it is an immense institution, one hundred laboratory places, two lecture halls, ninety-six chimneys [hoods?] and so forth—in short, it is a chemical miracle and I think when it is once finished you will not disdain to visit us. The arrangement remains the same: in a smaller room is the so-called six-hour laboratory for pharmacists under the direction of Fittig; in a large room is the twenty-four hour lab course of Geuther and von Uslar, and finally in another the daily one under Wöhler's direction where I have the honor to be. By winter the middle building and right wing will be done, *i. e.*, the auditoria and Geuther's part. We will then go somewhere or other and our room will be completed. By next summer everything will probably be fixed and ready.

As for the chemical conditions, first, old Wöhler is the same good-natured and benevolent man—unfortunately somewhat pedantic—but that is now never otherwise in Göttingen. However, his experience is extremely valuable and anyone interested in rare metals would find here a most glorious opportunity to work, for there is no lack of material and besides our old fellow has seen and tested an enormous amount. We have selenium by the kilo and pounds of tellurium—the platinum metals here constitute quite ordinary work for laboratory students, likewise with tungsten and molybdenum.

Limpricht's real successor is Geuther, that is, he lectures on organic chemistry using Wöhler's outline—a book which old Wöhler himself no longer employs. Geuther's following is slight. Whose child he is mentally you have perhaps seen from the truly miserable recent publication (CO on sodium alcoholate, electrolysis of SO_3, $AgO \cdot PO_5$, AsO_5, and so forth). He was formerly a very genial person, but now he is so surly and fierce that he often becomes unbearable. His constantly being checkmated in theories, the limited approval in which he finds himself here, and finally indeed even my appointment may have changed him into this unpleasant, grumpy, hateful disposition. Often enough he comes running into our laboratory, gossips with one or the other of the laboratory students and tries to make propaganda but it won't get him anywhere.

Von Uslar, of famous memory, is a former apothecary—a fool of the best kind—he previously had the six-hour lab course and lectures (or did) in analytical chemistry. . . . . .

Fittig has the six-hour lab course and is a former schoolmaster; he has never gotten out of Göttingen at all and considers Limpricht next to Wöhler as the greatest chemist of this century. He is completely the pedant through and through and treads so closely in the footsteps of his great teacher Limpricht that I consider him to be the most insufferable man I have ever met. He is now trying to become a tutor in analytical chemistry in order to compete with von Uslar. The present lecture assistant has fallen ill and Fittig has temporarily taken over his job so I have this monster in my place the whole day.[5]

As far as the other chemists, such as Wicke and Bökeker are concerned, they do not count; they each have their limited activities and practically do not come in contact with us at all.

Gerding—a writer who had got starved out of Prussia—has come here to establish himself as a lecturer. He had a family nearby, however, and was refused by the faculty. He holds popular lectures for outsiders and the general populace and announces private hours which, however, never take place.

Now for that which concerns my insignificance—it is clear from the strength of my position that I expect to habilitate myself here—I shall, however, allow the summer to pass and not go through the necessary changes until winter so that I shall not begin to lecture until the following summer. I expect to announce organic without delay and with the malicious addition, "According to the Newest Standpoint of Science." From that moment it will be my most zealous endeavor to "kill" my rival cold which I trust will not be difficult for the good God has placed a fluent tongue in my mouth and my friend Geuther is tongue tied.

As far as my research is concerned, I am at the end of the investigation of chlorobenzene [benzal chloride] which is nothing other than chlorinated benzyl chloride or bichlortoluene—very interesting, isn't it? Now, if, however, benzol alcohol is not benzyl glycol, then another substance must have this constitution. This other material is, however, saligenin which also is now being studied. Unfortunately I have been able to prepare no protochloride in order to bring out the striking isomerism—saligenin with PCl_5 splits into saliretin and water just like salicylic acid. Saliretin is resinous, however, and for that reason vigorously resists the action of excess PCl_5. Nothing remains other than to prepare esters, although these are so unstable that for example acetic anhydride completely resinifies saligenin. Salicyclic acid remains my last hope that according to the principle of similarity a stable compound will result. Even ethyl iodide resinifies saligenin.

Geuther has taken up work on chloroacetic acid and expects to prove that it is *dibasic*. . . . . In our place the observation has been made[6] that oxamide boiled with ammonia yields great quantities of oxamidic acid—in addition we are always messing around with selenium, and Wöhler has been able to prepare amyl telluride.

Now comes the real reason for this writing. You had in Heidelberg a very convenient apparatus for the preparation of anhydrous phosphorous pentoxide [phosphoric acid?] although I cannot recall the details and little tricks about it. You would be doing me a very great favor if at your convenience you would send me a description of it. I shall always be glad to reciprocate.

In setting up the new place we four colleagues held a conference. All of my co-workers have not yet gotten away from Göttingen—the men have no idea of improvements and as I make, one after another, a series of proposals for purchases I encounter the most vigorous opposition. The donkeys regard almost everything as superfluous. Berthelot's apparatus for heating sealed tubes has been approved, but of a gas furnace for organic combustions they would hear absolutely nothing. Von Uslar said that Mendius had written him from Heidelberg that Bunsen had completely given up using gas for combustions. I had recommended the Bunsen furnace and incidentally Heintz's from the tests at Breslau and because of Erdmann's warm recommendation. What an idea—they will keep on using coal. Meanwhile I have not given up my intention, and if the laboratory does not purchase a furnace, I will buy one myself. I have written to Heidelberg, but as yet have received no answer. Have you heard anything about giving up gas furnaces? The thing is not yet settled and since I have lined up with the architect I hope to put a good deal through in spite of all the opposition. You have had experience and made many observations—if you know of any tricks or improvements, tell me about them and I will be forever in your debt.

But enough of *us*—how are *you*? Have you been able to get a lot done? What about the book? That the first part has been well received I probably do not need to tell you—but the sequences should follow one another rapidly—of course as compared with eternity, a year is only a short time. Just be sure that your book isn't like the Cologne cathedral, for already nitrogen is being regarded as pentavalent. Limpricht's first half is also out; the second is being delayed because he is getting ready to lecture in inorganic chemistry and there is little time left for writing. Besides he is absorbed with the building. Schlossberg is crafty in that matter; while others give out their work drop by drop he comes out with a great thick opus all at once.

What is Baeyer up to? I have heard nothing from him. Well, farewell and write to me soon. I hope that you are touched by this long epistle and before another Sunday morning passes will send me a few lines. I should be glad to hear news from outside for here I go around with no one but my colleagues (and that is as good as no one) for I have the strictest orders from the old man [Wöhler] to get along well with my companions.

F. BEILSTEIN
Your ever devoted servant

MARKET PLACE
HOUSE OF MERCHANT HENKE

[5] Mr. Richter informs me, however, that inspection of Fittig's diaries shows that Beilstein's prejudice was soon replaced by warmer feelings and that later on the two men were attached by a close friendship [*cf. Ber.*, **44**, 1351–2, 1355 (1911)]. At the time of writing this letter Beilstein had but just arrived at Göttingen, and the harshness of his statement must be attributed to his youth and the very different temperaments of the two men.

In contrast to the wanderings of the first two periods of his career the third was passed entirely in Russia. In 1866 he was invited to succeed Mendeléeff at the

[6] TOUSSAINT, *Ann.*, **120**, 237–41 (1861).

Imperial Technological Institute of St. Petersburg where he subsequently taught for thirty years. In 1887 he was elected a member of the Imperial Russian Academy, which honor carried with it a good income, a private dwelling, and a laboratory. He was thus soon able to retire from his professorship and devote himself entirely to research and to the development of his "Handbuch."

BEILSTEIN'S EXPERIMENTAL CONTRIBUTIONS

Although now somewhat overshadowed by the eminence of his well-deserved fame as the author of the well-known "Handbuch," Beilstein's experimental and theoretical contributions to the development of organic chemistry were substantial. Although the last seventeen years of his life were devoted exclusively to this literary work, yet during the period of thirty-three years from 1856–89 he published more than a hundred experimental contributions in German and French journals alone, not to speak of many in Russian; although neither time nor space permits here a detailed analysis of his experimental contributions, a few of the more outstanding items may appropriately be mentioned.

During his year in Paris with Würtz, Beilstein studied the action of phosphorous pentachloride on acetal and demonstrated[7] for the first time that the dichloro product obtained (ethylidene chloride) was identical with that resulting from the action of PCl_5 on acetaldehyde (Würtz, Geuther) or from further chlorination of ethyl chloride (Regnault). In 1860 this observation suggested to him a comparison of chlorinated benzyl chloride (benzal chloride) with the product obtained from benzaldehyde by the action of PCl_5. This pair also proved to be identical, and he was, therefore, able to conclude that when PCl_5 reacts with an aldehyde the chlorinated chloride of the corresponding alcohol is produced (*i. e.*, the oxygen is replaced by two chlorine atoms). Some years later (1866) an extension of this study on the halogenation of toluene led Beilstein to the very important discovery[8] that the further chlorination of benzyl chloride yields different products according to the temperature used. With boiling toluene, chlorine gave benzyl or benzal chlorides; at ordinary temperatures the chlorine substituted one [one more] of the nuclear hydrogens. This difference was detected by oxidation of the two types of products, the one yielding benzoic acid, the other chlorobenzoic acid. This very important discovery had previously been overlooked, not only by Cannizzaro (the discoverer of benzyl chloride) but even by Beilstein himself, because neither had taken care to cool their reactions, and, as a result, the evolution of heat had been sufficient to yield only side chain halogenation. The discovery of the influence of temperature in controlling the nature of the substitution has, of course, been of the utmost importance to industrial organic chemistry.

As a direct result of his necessity for testing for the presence or absence of halogens in his materials Beilstein devised[9] the beautifully simple procedure now constantly employed in all laboratories under the name of the *Beilstein test* for halogens in organic compounds. Combining the known oxidizing action of copper oxide on organic compounds with the relatively volatile character of the copper halides and the characteristic color which they impart to a flame, Beilstein tested for halogens by merely dropping a bit of organic material onto a small quantity of powdered copper oxide held in a loop of platinum wire over a Bunsen flame. If chlorine, bromine, or iodine is present in the original organic material, the resulting blue-green flame quickly betrays its presence.

Perhaps because of his close personal friendship with Kekulé and his consequent natural interest in the development and application of the famous hexagonal benzene formula, Beilstein carried out a long series of fruitful researches on the isomerism of substituted benzoic and other aromatic acids. He was the first to prepare *p*-nitrobenzoic acid;[10] he first recognized that during the nitration of cinnamic acid there is formed in addition to the main para isomer a certain amount of *o*-nitrocinnamic acid and that this is the source of the indole which Baeyer had obtained by fusion of the crude nitration product with caustic potash and iron filings. Although the use of tin and hydrochloric acid for the reduction of nitro compounds had already been suggested by Roussin, Beilstein demonstrated its superiority to the other means then in common use and that with polynitro compounds it was able to reduce all nitro groups to amino groups.

Toward the end of the 1860's there was great uncertainty about the various nitrotoluenes. There was known a solid (*p*-nitrotoluene) and a liquid (*o*-nitrotoluene) but the homogeneity of the latter was still doubted. Rosenstiehl discovered that its reduction product was a mixture of two amines and therefore that two (or more) nitrotoluenes are obtained by nitration. This was confirmed (1870) by Beilstein and Kuhlberg, who found that the liquid nitrotoluene gave the liquid toluidine and who also prepared it from 2,4-dinitrotoluene by partial reduction and subsequent elimination of the amino group. In addition to characterizing the two principal mononitrotoluenes they first prepared the third isomer (*m*-nitrotoluene) both from *o*-acetotoluidide[11] and *p*-acetoluidide[12] by nitration, and subsequent elimination of the amino group.

Upon his return to St. Petersburg (1867) he became a member of the Imperial Russian Technical Society and in this connection undertook the investigation of the characteristics of Caucasian petroleum. Quickly finding that its density was no measure of its value, he further discovered that under the conditions then em-

[7] *Ann.*, **113**, 110–2 (1860).
[8] *Ibid.*, **139**, 331–42 (1866).
[9] *Ber.*, **5**, 620–1 (1822).
[10] WILBRAND, BEILSTEIN, *Ann.*, **128**, 257–73 (1863).
[11] *Ibid.*, **158**, 346 (1871).
[12] *Ibid.*, **155**, 24 (1870).

ployed it actually gave some ten per cent. more illumination than the imported American variety. Public prejudice against the domestic product was then soon dispelled, and interest in the development of the Russian industry markedly accelerated. Upon further study it developed that the Russian petroleum contained less hydrogen than the American and that its components had a composition corresponding to the empirical formula C_nH_{2n}. Presently it was found that these hydrocarbons were identical with the hydrogenation products of the aromatic hydrocarbons, and Beilstein was able to isolate hexahydrotoluene from the Russian oil. These and other allied observations were quickly followed up by others and led in 1883 to Markownikow's systematic study of what we would call naphthenes.

These few illustrations selected from the voluminous mass of his published experimental work perhaps suffice to demonstrate that Beilstein is entitled to fame on these grounds alone. However, these fundamental discoveries which today constitute the foundations of our organic edifice are overshadowed by multifold extensions and ramifications of organic chemical practice and theory. We are so intent upon recent developments that rarely do we give ourselves the privilege of examining the experimental labors of our predecessors. Small wonder, therefore, that Beilstein is doubtless much more widely known to our contemporaries through their constant daily employment of the modern version of his "Handbuch der Organischen Chemie."

THE EVOLUTION OF THE "HANDBUCH"

Beilstein began at Göttingen to assemble the material which ultimately came to be the famous "Handbuch." At first his notes on the current literature were probably prepared merely to facilitate his own personal research. At least he is not known to have indicated to his friends that he had in mind any such comprehensive enterprise as it has since become. It may well have been that during the course of his editorial work for the *Zeitschrift für Chemie* he gradually evolved the idea of integrating his own records of the existing literature into some kind of systematic compendium. At any rate by the time of his removal from Göttingen to St. Petersburg the preparation of such a handbook had become a definite objective and his work upon it continued with increasing fervor.

Although in some respects Beilstein was not entirely pleased with Russian educational conditions, nevertheless they did have the effect of giving him more opportunity to work at his "Handbuch." In a letter to a German friend he wrote,

> "To be sure I could write my 'Handbuch' only in Russia and therefore I have declined invitations to come back to Germany. At a Russian technical school the professors need not undertake research for here it carries no weight with the students, but in Germany this would be regarded askance."

So after the regular laboratory work of the day was over Beilstein continued quietly at his writing table day after day and year in and year out. Gradually the gaps were filled in and toward the end of the seventies the manuscript was finished. He found an interested publisher in the firm of Leopold Voss in Hamburg, and beginning in 1880 the manuscript whose preparation had occupied more than twenty years began to appear in print. Due to the fact that its author had approached no publisher until his material was virtually complete the one hundred ten signatures which constituted the two volumes of 2201 pages came from the press in rapid succession and within two years the first edition was complete (1880–1882).

That the chemical world was quick to recognize the value of its new tool was demonstrated by the complete exhaustion of the first edition within a few months. The publishers, of course, wished to proceed at once with another printing. To this natural desire, however, Beilstein interposed vigorous objection. He recognized that a work of such magnitude must inevitably contain numerous errors, not only those of mere typography but those due to misunderstanding of or lack of clarity in the original papers. Both in private correspondence and in a letter published in the *Berichte*[13] he begged for the assistance of all chemists in discovering and correcting possible inaccuracies. After some years of additional labor devoted to corrections, improvements, and the incorporation of new material a second edition was published. This had grown to three volumes of two hundred fifty signatures with a total of 4080 pages, but like the first appeared rapidly so that it was complete between 1886 and 1890.

It has been said that apparently Beilstein took a certain pleasure in saying that for his work he had a special office and staff of collaborators. This was just his own little joke for actually his office consisted only of his own workroom in which, surrounded by journals, manuscripts, and corrections, he sat at his writing table or typewriter. He himself examined all the chemical journals and edited all editions of his work with the help of only one assistant. He once described his procedure as follows:

> "I read everything and enter it where it belongs."

Rarely was he separated from his manuscripts and editorial papers. They even accompanied him on his travels and often exercised a decisive influence upon the place selected for vacations. In 1896 when preparing to spend the summer in Finland he wrote to his friend, Hjelt,

> "I would be sorry to locate too far away from Helsingfors. I must continue work on my 'Handbuch' even during vacations and am therefore under the necessity of referring back and forth in the library. In Baden-Baden this was very easy, for in half an hour I could reach the Polytechnikum in Karlsruhe where I found everything."

Even before Beilstein undertook the preparation of a third edition it had become evident to him that the

[13] *Ber.*, **17**, 489 (1884).

task was becoming too great for his strength. The abundance of material and its classification according to the original plan seemed to him increasingly more difficult. A complete revision of the method of classification, particularly for the cyclic compounds, appeared imperative.

"To reclassify and revise the huge amount of material," said he, "would require years of preliminary work and at my age [he was about fifty-five] it is doubtful if I should be able to complete it all."

In order to avoid any long interruption of the publication, however, he determined to proceed with a third edition which should be revised only in the most necessary parts, and to which new material could be added in the form of a supplement. In the meantime, however, he initiated steps toward the continuation of the work and in January, 1895, authorized his publishers to approach Professor Paul Jacobson of Heidelberg with an invitation to undertake the continuation of the work, beginning with the preparation of a supplement to the third edition.

Recognizing that with the rapid growth of the literature the magnitude of the task would soon overwhelm any private enterprise, Jacobson felt obliged to decline. He did, however, offer an alternative proposal according to which the preparation of abstracts for the *Berichte*, the publication of the *Jahresbericht*, and the preparation of the Beilstein "Handbuch" would be consolidated in one central bureau under the auspices of the German Chemical Society. Although at first disappointed at Jacobson's unwillingness to take over the work personally and cool to the alternative proposal, Beilstein shortly thereafter did suggest that the German Chemical Society take over the publication of the "Handbuch" and offered to convey to it all his rights as author. Under these circumstances the directors of the society voted on November 30, 1895, to undertake the continuation of the "Handbuch" and at the same time the publication of the *Centralblatt*, the abstract section of the *Berichte* being discontinued. Subsequent to certain necessary statutory changes authorized by the general assembly of June 19, 1896,[14] this arrangement became effective as of January 1, 1897. Beilstein turned over to the German Chemical Society all material then in his hands and Jacobson (who in the meantime had become the first general secretary of the society) became editor of the Supplement to the Third Edition of the "Handbuch".

Beilstein was now happy that the continuation of his life work had been placed in sympathetic and competent hands. He wrote to M. M. Richter,

"I can now pass quietly from the scene for I am certain that my work will be kept up in the best possible manner and that chemists more than any other type of investigators may be assured of good and complete handbooks at reasonable cost. The German Chemical Society has inherited the 'Handbuch,' and I trust that all chemists will approve of this disposition."

[14] *Ber.*, **29**, 1615–7 (1896).

Meanwhile he completed the main part of the third edition which appeared between 1892 and 1899 in four volumes of 6844 pages. In its preface he says,

"The consciousness of having laid the foundations for such a work is the best reward for almost forty years of labor and will be for the rest of my life a source of inner satisfaction."

Under the new arrangement the editing of the supplement to the third edition went rapidly forward and immediately after the completion of the main part the supplement began to appear. Indeed, at one time Beilstein began to be afraid that the supplement would get ahead of the main edition. In February, 1899, he wrote to Richter,

"In the meantime Jacobson is vigorously at work and his driving energy pushes him constantly along. I have had to write to the directors of the German Chemical Society suggesting that it slow up a bit for otherwise the gentlemen in Berlin will begin to print supplements before I have completed the main part."

Nevertheless, he was immensely pleased at the promptness with which the supplement appeared and the excellent work of the new editorial board. In January, 1906, he wrote,

"I await with impatience the appearance of the general index. [Volume V of the supplement]. Only when I see this shall I be able to breathe freely and to say that all is now complete and I can pass out of the picture."

It almost seems as if this were literally true for the work was finished in October, 1906, and on the eighteenth of that month he passed away.

Now that the specific objective set by the German Chemical Society in 1896, had in ten years been reached by the completion of the third edition and its corresponding supplement the question of the future of the undertaking had to be decided. The possibility of issuing a second supplementary series was contemplated, but since even Beilstein himself had recognized the necessity for devising a completely new classification this solution did not appear attractive. In May, 1906, Jacobson reported to the directors of the society that such continuation of the supplement was definitely inadvisable and recommended the preparation of a completely reorganized fourth edition. Although his preliminary estimates indicated that such an edition would require at least 16,000 pages and some sixteen years of preparation the society determined[15] to undertake the enterprise. To Jacobson and Bernard Prager were committed the editorial responsibilities and reports of their progress were made annually to the society.[16]

During 1907 a completely new system of classification was devised which was printed for the guidance of the editors in a volume of one hundred thirty-three pages. Next followed (1908–12) five years of labor devoted to the recasting of the old material according

[15] *Ibid.*, **39**, 4449–50 (1906).

[16] *Ibid.*, **40**, 5028 (1907); **41**, 4489 (1 908); **42**, 4923 (1909); **43**, 3626 (1910); **45**, 698 (1912); **46**, 638–9 (1913); ***47**, 600–1 (1914); **48**, 298 (1915); **49**, 626–7 (1916); **50**, 313 (1917); **51**, 489 (1918).

to the new system. It then became necessary to decide whether to work up the literature to one definite date which should be the same for all volumes or to carry each volume as closely as possible to the date of its publication. On the expectation that the former plan would facilitate the publication of the work in about seven years (rather than fourteen by the alternative) it was decided that the fourth edition should in all volumes bring the survey of the literature up to January 1, 1910.[16]* The editorial work for this required from 1913–16 so that ten years of labor were required before even a single character could be printed. All this expense naturally presupposed much more financial support than could possibly be afforded by the German Chemical Society alone and the enterprise was underwritten by a special association formed for the purpose. Despite the outbreak of the World War, by the middle of 1916 the entire file of material was assembled in one hundred twenty-three fireproof filing cases in the Hofman House in Berlin. To protect the valuable manuscript from possible loss it was photographed in manuscript form. In December, 1916, the first volume was sent to the printers and despite the lack of compositors and the scarcity of supplies the first volume was finished by the end of 1918 on faultless paper and with a pleasing and satisfactory binding.

The new classification system employed in this fourth edition is based on the premise that every definite organic compound can be expressed by a structural formula. Three of the four main divisions of the system correspond to the nature of the skeleton of this formula, *i. e.*, according to whether the compound is acyclic, isocyclic, or heterocyclic. The fourth division comprises natural products of indefinite composition or incompletely known structure. It is of timely interest to report that the "Handbuch's" treatment of the literature up to January 1, 1910, of all organic compounds of known structure has just been completed and represents twenty-seven substantial volumes issued over the period 1918–37 inclusive. To deal with the literature from 1910–19 inclusive there is also a corresponding set of supplementary volumes, twenty-six of which have already been published and the twenty-seventh and last of which is expected momentarily. In a few instances several of these supplementary volumes are contained within a single binding, but it is perfectly fair to say that the main fourth edition and its first supplement comprise fifty-four magnificent volumes aggregating more than 30,000 pages. A second supplementary series to cover the literature since 1920 has already been authorized by the German Chemical Society.

This development of Beilstein's modest initial venture into its present monumental form through more than thirty years of continuous effort constitutes an accomplishment of which any professional society may well be proud. As an achievement in the patient execution of a great coöperative contribution to the progress of chemistry it constitutes an almost unparalleled example. American chemists have been quick to appreciate not only the indispensable utility of the work as a whole but particularly the beautiful simplicity and ingenuity of the fundamental plan of the new classification. Already one great American chemical corporation has adopted for its research laboratory a filing code based entirely on the Beilstein system. This is used for filing all samples of organic compounds, patents, research reports, correspondence, and miscellaneous information relating to organic compounds. Thanks to the patience and ingenuity of its devisers organic chemistry now possesses a tool which not only provides for all compounds already known but is capable of indefinite expansion to the untold millions yet undiscovered and unknown.

The Beilstein "Handbuch" is so dear to the organic chemists that it is small wonder that they should memorialize it in song. Under the title of "Einleitung in die organische Chemie" on Page 595 as No. 658 of the 91st–95th editions of Schauenburg's "*Allgemeines Deutsches Kommersbuch*" there appears the following jingle (words by Erwin Sack) to be sung to the tune of "Die Wacht am Rhein."

Dinitrobromanthraquinon,
Alphaphenylacrosazon;
Benzol toluol zylol naphthol,
Phloroglucin guaiacol,
Propylamin butylamin,
Sodiumisophthalat trichlorhydrin.

Nitrophenylacetylen,
Arabinose fluoren;
Ethan propan butan tolan,
Trioxytriphenylmethan,
Oxyisoamylamin,
Heptachloranthracen anthrarufin.

Ammonium carbaminat,
Sodium antimonyl tartrat;
Strychnin brucin cinchonidin,
Quinin morphin papaverin,
Formal chloral bromacetal,
Maltose galaktose methylal.

Dithioethylenglycol,
Methylsulfid benzthiazol;
Fuchsin aurantia aurin,
Ponceau bordeaux tropaolin,
Imidodimalonimid.
Indoxyl oxindol rhamnodulcit.

Paraacetphenetidin,
Dimethyloxychinizin;
Phenol thymol orcin iodol,
Phenose tetraiodpyrrol,
Alphaphenylpropionitril,
Trinaphtylcarbinol dipropargyl.

About the turn of the century there was a New York Section of the Verein Deutscher Chemiker which held its formal meetings jointly with the New York Section of the Society of Chemical Industry in the auditorium of a rented building at 108 West 55th Street. The real meeting of the Verein, however, was always held subsequently to the S. C. I. meeting and consisted of beer, pretzels, and songs. It was at these later meetings that the Beilstein song was used.*

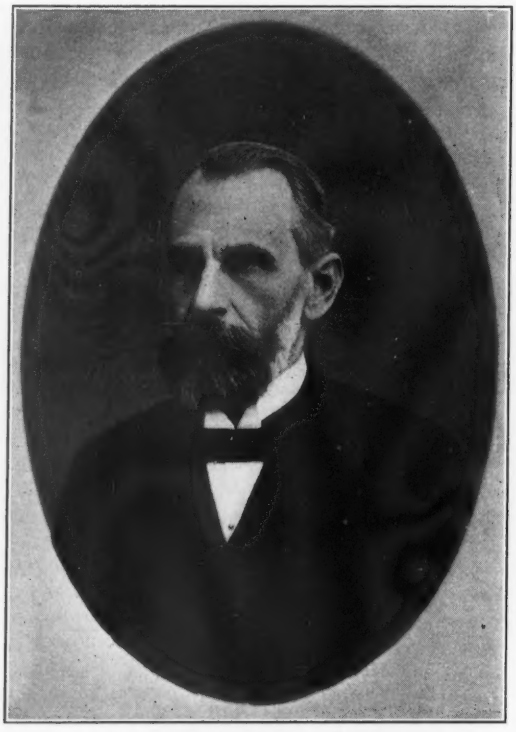
* For the account of these circumstances and for the words of the Beilstein song I am indebted to Dr. D. D. Berolzheimer who published it in "The Percolator" of the Chemist's Club some twenty-five years ago.

HOW BEILSTEIN IS MADE*

FRIEDRICH RICHTER

Editor of "Beilstein's Handbuch der organischen Chemie," Berlin, Germany

"OUR last recourse must be had to large Indexes and little Compendiums: Quotations must be plentifully gather'd and book'd in Alphabeth: To this end, the Authors need little be consulted, yet Criticks, and Commentators, and Lexicons carefully must."—How many books have not been written in accord with Swift's amusing prescription, but their fame was usually of short duration and today they moulder forgotten on dusty shelves. It is worth a moment's reflection that a comprehensive, scientific work like the Beilstein "Handbuch" has shown undiminished vitality through more than fifty years of our swiftly moving times, while the name of its founder sounds almost mythical to the present-day chemists. A short history of this work and the method of compiling it seems distinctly worth while.



BEILSTEIN IN 1892

The editors of chemical handbooks have always had worries. Perhaps one of the first to experience these was Diderot, who omitted most of the promised chemical articles from his encyclopedia. Macquer, the editor of the first alphabetical dictionary of chemistry, in 1776 wrote concerning the second edition to Guyton de Morveau, "You know what the condition of chemistry is today: Only a child two days ago, it suddenly finds itself in an incredible state of growth, and is changing into a colossus." Few references to the literature were given in this work and only the patient diligence of the German translator, Leonhardi, converted it into the invaluable source from which the chemical historian still derives much information. Ten years later, when Guyton de Morveau attempted in the "Encyclopédie méthodique" to give a complete presentation of the chemical knowledge of his time, he had to insert a new preface in the middle of the work to announce his conversion to the Lavoisierian theories and defend himself against the charge that he had made a "hurried compilation." In 1841 Wöhler wrote to Berzelius concerning Leopold Gmelin, who in 1819 brought out the first handbook of organic chemistry, "He is in despair as to what system he ought to use for organic chemistry." Gmelin died in 1853 in the midst of preparing the fourth edition of his organic chemistry. This was so hopelessly outmoded within ten years that it survived no further editions.

The history of science knows no standstills and famous textbooks mark its course like milestones. When (1881–83), scarcely thirty years after Gmelin's death, Friedrich Konrad Beilstein (1838–1906) put out the first parts of his "Handbuch der organischen Chemie," he could not have foretold that this modest attempt, as he called it, would make his name immortal. From the two small volumes of the first edition it could not have been foreseen that eventually forty volumes would not suffice to house the total treasure trove of organic chemistry.

It is not certain when Beilstein conceived the idea of publishing his work. It is only known that it was the fruit of more than twenty years of collecting memoranda for his own use. This activity can doubtless be ascribed to the motives so well expressed by Berzelius in his letter of March 5, 1831, to Wöhler, "The professor complains of excessive writing. Of course this is boring, but we must admit that without this writing one never attains his potentialities. If, for instance, Davy in his youth had been forced to write, as the professor now is, I am convinced that he would have advanced chemistry by a whole century: but under the

* Translated by Ralph E. Oesper, Associate Professor of Chemistry, University of Cincinnati.

circumstances it became nothing more than 'brilliant fragments,' just because, from the beginning, he was not forced to diligently familiarize himself with all parts of the science as though it were a unit."

The first edition of Beilstein's "Handbuch" was sold out almost immediately—clear testimony that his personal need for an ordered collection of the facts was shared by many others and that the time was ripe for a work of this kind. The second edition followed quickly in 1885, the third in 1892. When Beilstein, with the third edition, closed his participation in the "Handbuch," he left "a stupendous monument of industrious, intelligent compilation" (Bolton). He wrote to a friend, "If in quiet I now review the achievements of my last forty years, it occurs to me how fortunate I was to have been born at a time and to have lived in a period when such an undertaking as my Chemistry could be accomplished. By chance, all the favorable conditions coincided. A delay of only a few years, and all would have been in vain."

What were these favorable circumstances? The first, his untiring diligence, he modestly did not mention. Hjelt, in his biography of Beilstein,[1] tells that Beilstein did not allow vacations to interrupt the work on his "Handbuch." This unceasing concern for his work is illustrated by an amusing experience related by his assistant, Wihtol. On high feast days and similar occasions, Beilstein sat well behaved with his relations in the church pew. However, a glance over his shoulder revealed on his opened hymn book a very long chemical formula: the book concealed a proof sheet of the "Handbuch." In this way, he provided, as the Russians say, that "the wolves were sated and the sheep remained whole." More important is a second circumstance through which the "Handbuch" became a memorial of a special kind. A glance at its forerunner, Gmelin's "Handbuch der organischen Chemie," suffices to show the far-reaching change that had occurred in organic chemistry between 1860 and 1880. This change was primarily the work of Kekulé, who had laid the firm foundation of the modern science with his structure and benzene theories. Until then the multiplicity of organic compounds had been a rather confused mass of empirical results: now appeared the first contours of a newly ordered world. Hardly more than ten years were necessary for the almost general adoption of the method of writing formulas still used today.[2]

Beilstein's work was the first complete compendium of organic compounds written in the spirit of this new viewpoint. It was a test of Kekulé's ideas and the fact that it could be carried up to the present without essential alteration argues for the solidity of these theoretical bases. This is the second favorable circumstance leading to the continuance of the "Handbuch."

Beilstein also made some experimental contribution to the development of Kekulé's teachings. He wrote, "My critics reproach me with having accomplished little of real significance along this line, but it was necessary to show beforehand that there is only *one* benzoic acid, that benzyl chloride and chlorotoluene are different, and so forth, before these could bring to your theory that range and that significance which it had from the beginning." Kekulé readily acknowledged this aid.

Today Beilstein's literary accomplishment appears incomparably greater than his experimental studies. It is really astounding that he compiled three editions of his work with practically no assistance. In May, 1895, he wrote to one of his German friends, "Obviously I could write my 'Handbuch' only in Russia, and therefore I declined all calls to Germany.[3] At a Russian polytechnical school the professors need not be scientifically active because even the students arouse no such impulse, but in Germany I would have been viewed askance."

The avalanche-like extension of the literature toward the end of the century rendered impossible the continued compilation of the "Handbuch" by a single individual. In 1883, shortly after the closure of the first edition, M. M. Richter estimated there were only 15,000 organic compounds. By 1910 this number had risen to 150,000. The figure for today is somewhat uncertain, but 350,000 cannot be far wrong. Consequently, it was a further happy circumstance in the history of the "Handbuch," that the German Chemical Society, under the active leadership of its Vice-President, Emil Fischer, in 1896 was ready to assume the responsibility for the work and to establish a separate editorial office for its continuance. This made possible the publication of the supplementary volumes to the third edition (1899–1906) and the issuance of a fourth edition (1918 on). Of course, even these beginnings were still quite modest because the entire editorial staff at first consisted of an editor and one assistant. However, everything was on a completely new basis in so far as the staff no longer needed to concern itself with culling the literature, that is, in a sense, with providing its "raw materials." This was due to the happy thought of entrusting this task to the abstractors of the *Chemisches Zentralblatt*, which had been taken over

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[1] HJELT, E., *Ber.*, **40**, 5041 (1907); for other biographical sketches see LUTZ, O., *Z. angew. Chem.*, **19**, 2058; WITT, O., *J. Chem. Soc.*, **1911T**, 1646; GAUTIER, A., *Bull. soc. chim. Fr.*, [3], **35**, 1 (1906).

[2] It is of historical interest to note that at first Kekulé did not know how to escape entirely from the type theory. "They (the type formulas) disclaim the ability of expressing the way in which the carbon atoms themselves and the atoms of other elements completely united with them are joined; the reason being that complete disintegration of the radicals leads to such complicated formulas that all clarity of arrangement is lost." (Kekulé, *Lehrbuch* II, 250.) On this occasion Beilstein proved himself the keen critic foreshadowing the future author of the "Handbuch." In a letter to Kekulé, Oct. 3, 1865, he writes, "Please, please, throw the types out. Remember the old saying: *formulae non agunt nisi solutae*—Dissolve them then more drastically than in the famed phthalic acid formula. Build in your atoms [= molecules] or nuclei: grottoes, caves, arbors and gardens, so that the imagination of the chemists can fill them with the loveliest H, Cl, or other spheres, and their minds can be set at rest."

[3] Munich, 1868, Halle, 1881, and so forth.

by the Chemical Society at the same time. Useless duplication was avoided by placing the preparation of the *Zentralblatt* abstracts and the summaries for Beilstein in one hand. The staff needed only to check against the originals the correctness and the completeness of the abstracts delivered to it. This task in itself was still voluminous enough, but this procedure had the advantage that the staff acted as a second control and, to a great extent, eliminated the possibilities of error. This arrangement proved excellent for more than twenty years and was the basis for the preparation of the first supplement to the fourth edition. However, when the great growth of the post-war literature brought corresponding increases in the number of the *Zentralblatt* abstractors and, in addition, a more frequent turnover in the abstracting staff made its disturbing effects noticeable, the disadvantages began to outweigh the advantages. When the second supplement to the fourth edition was projected in 1928, the editorial staff was forced to reassume the abstracting of the original literature and to prepare all the memoranda slips in its own offices.

The raw material, with which the editorial staff works, are the single "Beilstein slips." The originals of about forty of the most important chemical and physical chemical periodicals are abstracted completely. The *Chemisches Zentralblatt* is the source for the rest of the literature. The unavoidable brevity of its abstracts requires that here also the originals must often be consulted. Each slip, in principle, bears statements concerning one compound only. The data are set down in a definite order: occurrence, formation, preparation, physical properties, chemical and biochemical behavior, analytical, the salts. Since, for technical reasons, every original paper must be abstracted separately, each slip contains statements from a single paper only. For the fourth edition of the main volumes these slips numbered 250,000. The correct abstracting of the literature and the checking of the slips for accuracy by no means completes this phase of the editorial task. The next important step is the arrangement of the file of slips in the order in which the material will appear later in the "Handbuch." Accordingly, on each slip is written the System Number which definitely determines the position of the compound in the completed volume.

The editors expended much labor in bringing this System of organic compounds to its present form. Of course, it was not devised from the ground up; it is the product of a long historical development. The fundamental ideas of homologous series, of parent nuclei, and functional groups have existed since about 1840; the distinction between cyclic and acyclic compounds was added in the sixties. These were the basic elements which sufficed Beilstein for the arrangement of the 15,000 compounds included in his first edition. When, however, about in the eighties, the number of heterocyclic compounds also began to increase considerably, Beilstein's original principles of arrangement were no longer adequate. He himself recognized that the invention of a new system would be one of the most urgent problems of the future. After laborious preliminaries the new system was finally ready in 1907. It has fully proved its merit in the succeeding thirty years, and, in all likelihood, will suffice for a long time.

The basic ideas, as the writer has shown elsewhere,[4] are by no means as complex as many still consider them. The division into acyclic, isocyclic, and heterocyclic compounds, and the arrangement according to homologous series and the degree of saturation is traditional and requires no further explanation. New and fundamental, however, is the idea that only the unbroken carbon chain[5] and the ring are regarded as significant with respect to the systematic viewpoint. The System deals primarily only with compounds of which this is true. These are the "index compounds." All others appear as their derivatives, which can be considered as arising by substitution, or by the loss of water from two or more index compounds. The loss of water or "anhydro synthesis" thus becomes the "systematically" most important reaction of organic chemistry. Those parts of the index compounds on which it occurs are the functioning groups. The exact definition of these (OH, CO_2H, NH_2, etc.) and their limitation to a not too large number (about twenty) is the real basis of the new system. If for a given compound the index compound has been determined, and the decisive functioning group and the degree of saturation fixed, then the System Number giving the place of the compound in the "Handbuch" can be found. Without exaggeration, these simple principles make it possible to arrange easily, or find, 70–80 per cent. of all organic compounds. Real difficulties are encountered only when the basic structural formula does not give the necessary precise single picture as, for example, when a choice must be made between numerous desmotropic formulas. This choice can only be schematic. The number of thoroughly investigated cases of desmotropism is exceedingly small in comparison with the possible cases, and the method of deciding by analogy is nowhere so questionable as here. Therefore, numerous cross references to the other possible forms are necessary. This places an undesirable burden on the reader and the editorial staff, but it is due to the present state of chemistry rather than to a fault in the System. The System is not deficient, but the present method of expressing formulas lacks the necessary preciseness. Similar quandaries arise with many dyestuffs and related compounds for which, as yet, admittedly no satisfactory structural expressions have been found.

This detailed discussion of the questions involved in systematizing this vast array of compounds is distinctly pertinent because it will become increasingly significant as their number grows, since nomenclature

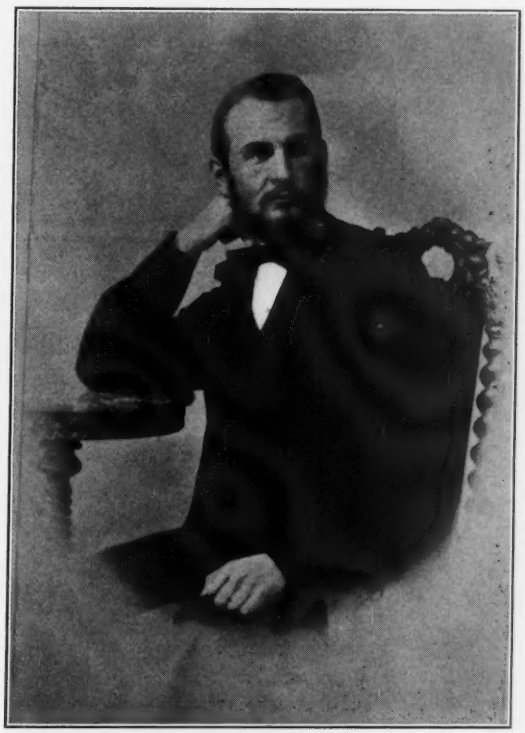
[4] RICHTER, FR., "Kurze Anleitung zur Orientierung in Beilstein's Handbuch der organischen Chemie," Julius Springer, Berlin, **1936.** See also E. H. HUNTRESS, "A brief introduction to the use of Beilstein's Handbuch der organischen Chemie," John Wiley and Sons, Inc., New York City, **1938.**

[5] Consequently ethers, sulfides, azo-compounds do not appear as special classes in the System.

and formula index can never be more than secondary aides.[6] The dislike of the practicing chemist for the System is understandable, even though he handicaps himself by this attitude. It is dangerous to foster the illusion that a better system may be devised in the future. Every conceivable system, of which there are many, will bring its own complications. Every system necessarily must depart from the simple ones used in the smaller traditional texts to which the practicing chemist is accustomed.

The System makes it possible to assign an unequivocal place to all organic compounds. This is of great moment, not only to the user, but it is also of the greatest importance to the editors. Many years intervene between the collection and the systematic arrangement of the material, but it must be possible at any given time to find immediately any given compound. Of course, it happens frequently that a recent publication may justify a new view of the constitution of a long known compound. If the reasons advanced appear convincing to the editors, new formulas must be entered on the slips at hand, and these must be arranged under the corresponding new System Number. Often this necessitates the reformulation of a large series of reaction products and a consequent transfer to other places in the System. This labor of Penelope would never end if a halt was not called by setting a time limit. Publications that have appeared after this date are, in general, not considered, but are held over for the subsequent supplementary volume. However, exceptions are made in special cases, particularly in the discarding of constitutional formulas recognized to be incorrect.

As soon as all the abstracts of a literature period are arranged systematically in the file, the work of the editorial staff enters a new phase: the assembling of the actual manuscript begins. This task varies considerably. Sometimes it consists in no more than slight stylistic changes, if the compound has been described only once and by a single author. When there is a more extensive literature which perhaps will fill one or more pages of the "Handbuch," the assembling of the individual statements into the finished article is anything but a mechanical task. Often it is found that the statements of different authors cannot be brought into satisfactory accord and the originals are carefully rechecked. Sometimes the disagreement is explained by slight differences in the experimental conditions. Such cases may arise easily because the abstractor, when preparing the slip, has merely the isolated fact in view, and so regards as unessential certain details which later prove significant when the total literature is under review. Frequently the literature contains actual contradictions: these require the Beilstein collaborator to take a critical stand. Such points have occasioned more than a thousand inquiries from the editorial board to the authors themselves. This correspondence has, in many cases, cleared up the incongruity, or sometimes further experimental studies are initiated. If the authors are dead the problem must be examined to determine whether one of the statements appears incredible in the light of present knowledge. Often it turns out that the statement is outmoded and that the method and discussion can no longer be accepted as conclusive. Sometimes it is possible to explain the true course of the reaction from parallel examples involving compounds of analogous structure. If all these measures fail, nothing remains but to present the conflicting statements side by side. The



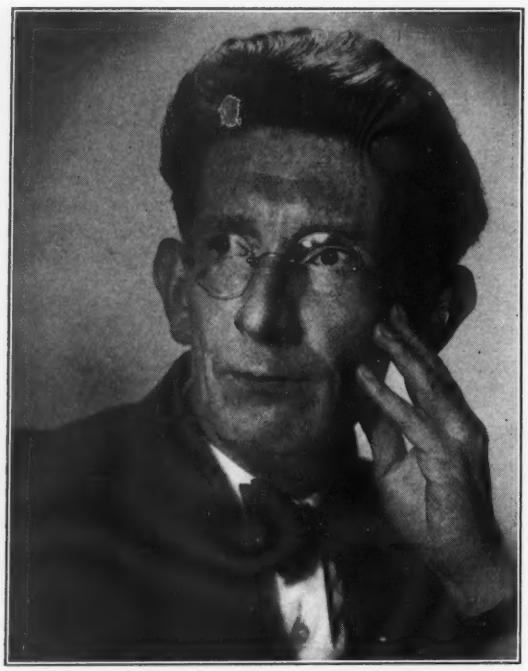
BEILSTEIN (AT GÖTTINGEN)

Beilstein collaborator is not allowed to exercise an arbitrary personal judgment.

The capabilities of the collaborator must measure up to high requirements in other respects. Although the "Handbuch" makes some claim to completeness, this does not signify that it includes every statement in the literature. In the older papers, especially, are given reactions which, considered from the present viewpoint, cannot succeed or which appear entirely without significance. The inclusion of such statements would merely clutter up the "Handbuch" and be of no value to the reader. In such cases, the collaborator, to a limited extent, must make a choice conditioned by the importance of the topic. For instance, obsolete methods must not be given in detail if it is now easier and cheaper to prepare the compound from other start-

[6] This was recognized quite some time ago. See EMIL FISCHER, "Aus meinem Leben," Julius Springer, Berlin, 1922, p. 136.

ing materials and by more efficient procedures. So far as possible, only the best should be taken from the welter of available physical data. It is well known that the figures given by the organic chemists of the older school are often not above suspicion. The principles to be followed in such critical choices have been excellently laid down by Timmermans.[7] This selection requires a large mass of comparative material and there are perhaps not more than fifty to one hundred compounds in all organic chemistry for which good



DR. FRIEDRICH RICHTER, EDITOR OF BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE

and bad physical data can be distinguished with certainty.

The critical presentation of the formation and reactions of a chemical compound, in general, involves complexities of which the layman has scarcely any conception. Every paper mentions, either as starting materials or reaction products, many compounds concerning whose constitution definite statements must be made. However, these compounds usually occur in widely separated parts of the "Handbuch" and can be subjected to an intimate, critical treatment only at a later time. This is possibly one of the most difficult tasks in the editing of the "Handbuch." At almost any instant the collaborator must be able to shift rapidly to another field, and, without spending too much time, make a provisional critical decision whether the starting material or reaction product under consideration will actually retain the formula assigned to it when this compound later is considered exhaustively.

The sciences bordering on chemistry, such as physics, medicine and technical chemistry, are considered in the "Handbuch" only in so far as they are of interest to the chemistry of the compound in question, and its use. Here, too, the collaborator often is faced with rather difficult choices.

These are but a few of the problems that must be solved by the editorial staff. The rules they must follow are exactly prescribed in numerous written directions, which fill many folders. Even so, the nature of this undertaking is such that a perfectly uniform editing of the manuscript is not attained. Consequently, several collaborators do nothing but subject the completed manuscript to another careful scrutiny to see that like chapters are treated alike, so that reactions mentioned under *Methyl Alcohol* are not omitted under *Ethyl Alcohol*, and so forth. Only after the manuscript has passed this stage does it come into the hands of the editor. He reads it carefully and verifies against the original literature anything which seems questionable to him.

Publications of the character of the "Handbuch," by their very nature, are bridges between the past and the future. From this fact arise, in equal measure, the difficulties and the pleasure of editing them. Mere accurate rendition of the literature and systematic arrangement would be sufficient to meet the requirements ordinarily demanded of an archive. Science, however, is a living organism which is continually developing and the observations from the past included in the "Handbuch" must serve the needs of the present. This means that the setting of a limiting date for closing the edition is merely a technical expedient, and the editorial staff must keep in constant touch with the present progress of the science. Here, as elsewhere, ability of high order is necessary to know what to omit. The findings of the past must be evaluated for the present and this appraisal must not be influenced by the fads that run their course in every science. But withal, the bounds of the whole must be set with good judgment so that room is left for the developments of the future. This is the point where the apparently purely reportorial activity of the editors merges into the creative, and the revision of the text with both these functions in mind is the last phase through which the manuscript passes before it is sent to the printer.

The correction of the proof of the Beilstein "Handbuch" is exceptionally laborious. The galleys are carefully compared with the manuscript to eliminate, so far as possible, numerical errors, all empirical formulas are verified once more, the index is prepared, and, lastly, the whole text is subjected to a last scientific review before it is finally released to the printer.

If the material set forth in Beilstein is surveyed, it becomes apparent that, in general, the co-workers cannot function as narrow specialists. However, the editorial staff does include specialists for certain topics,

[7] TIMMERMANS, J., "La notion d'espéce en chimie," Gauthier-Villars et Cie, Paris, 1928.

ONE OF THE EDITORIAL OFFICES

such as sugars, alkaloids, and so forth. This is true also of another field which has not yet been discussed: nomenclature. All the advantages and disadvantages of the chemical language are exhibited in the wide variety of names that can be given to even simple compounds. It would be impracticable to give in the "Handbuch" all the conceivable names for every compound. An intelligent selection is necessary. The chemical language, to a great extent, is founded on conventions. Therefore, the editorial staff is faced with the problem of determining which of these usages has shown itself likely to endure and to be capable of generalization. Such names are usually considered "correct." From these, whose number is still far too large, must be chosen those which are nearest the usages of the literature. An important point in the selection of names is that an understanding of the systematic arrangement should be facilitated by the names themselves. As can be seen, this involves an extensive classification, whose importance is just as great as the development of the System of organic compounds. Chemical nomenclature is as capable of change as the structural formulas themselves. It is an essential medium of expression, whose use must be cultivated carefully. At present, nomenclature is still the most important means of orientation for the user of the "Handbuch." This orientation will be made much easier by the forthcoming "General Index," whose publication may be expected within a few years. It is the writer's personal belief that orientation by the System is simpler than orientation by nomenclature. The chemical name, by its nature, is merely a restatement of the structural formula, and the number of formulas is much smaller than the number of names. The difficulties that must arise from the limited interests of the individual and the abundance of the material are obvious, so perhaps it is well that there are available several methods (including the formula index) by which the user can find his way through the mazes of the "Handbuch." The individual can decide whether he wishes to use nomenclature or the System as a guide, but he will have to choose one or the other.

The main volumes and the first supplement now (end of 1937) only lack the Main Division IV. It includes those natural materials whose constitutions, by January 1, 1920, had not been sufficiently elucidated to permit the inclusion of these compounds among the substances of established constitution. The chemistry of this group of materials has made rapid progress in the last fifteen years and the editorial board found itself faced here with a particularly difficult problem. Some of these materials, for example, the sterols and chlorophyll, have in this period taken on an entirely different aspect; consequently, the treatment of all these compounds could not be terminated with 1920. The tremendous additional work which this has imposed on the

staff is balanced by the hope that this volume, because of the abundance of its recent material, will bring the reader comparatively up-to-date information.

Another long-expressed desire of the chemical public will soon be filled. As has been pointed out, all the literature that has appeared since 1920 has been continuously abstracted by the staff. This task will be completed shortly and the first volumes of the second supplement may be expected in a few years. Then, for the first time, there will be a departure from the principle of a definite limiting date and the attempt will be made to narrow the gap between the literature and the publication date of each volume. This will meet numerous complaints. In the comparatively near future there will be accessible an orderly presentation of the entire material of organic chemistry.

The widening responsibilities of the editorial staff are best pictured by the constant growth in the number of collaborators. In his biography Hjelt wrote, "Many believed, as Beilstein often related with a certain satisfaction, that he had a special bureau with a staff of coworkers. This was anything but the case. His bureau consisted of his workroom where, surrounded by periodicals, manuscripts and proof, he sat at his writing table or typewriter. By himself he went through the whole literature, that is, all the chemical journals, and with the help of one assistant or secretary, he prepared all the editions of the great work." The changed conditions are apparent in the following Table:

	Editors	*Scientific collaborators*	*Technical collaborators*
1907	2	2	..
1918	2	6	..
1924	2	11	1
1928	2	24	2
1933	1	25	2
1937	1	27	3

It has been related of one of the great chemists (Wilhelm Ostwald?) that at the start of his career he made it a rule to read Liebig's *Annalen* from beginning to end, and he found this practice highly profitable for his scientific development. It is almost inconceivable that anyone might have the same idea with respect to "Beilstein." However, for about twenty years, the writer has found himself in the position of this imaginary "Beilstein reader." In closing, it may be of interest to learn something of the impressions of such a "Reader *malgré lui*." The "Handbuch" represents, to some degree, the microcosmos corresponding to the macrocosmos of living organic research. The attentive reader finds mirrored on every page the spirit of the science and its relation to human life. Two main endeavors are responsible for the abundance of organic compounds. From the needs of practical life arise the countless dyestuffs, medicinals, and other artificial products brought forth by the inventive genius of man. Among these are many compounds which have been studied little beyond the stage demanded by their practical application; they testify often enough to technical failures and fruitless wanderings into blind alleys. By the side of these materials stands a stately host of products which have been the subject of thorough scientific investigations. This pictures clearly the fact that pure science often is the child of technical empiricism, that it frequently then goes its own way along the path of purely academic research, and finally returns proffering its knowledge to service the needs of daily life. There is the equally numerous host of compounds that bear witness to the search of the inquiring human mind concerning the material foundations of natural phenomena and life processes. It would be hard to find a more impressive example of the essence of a science than the immense number of compounds which have been assembled as building blocks for the orderly erection of structural chemistry. Proof of structure was the incentive for the preparation of a very considerable fraction of the organic compounds. This edifice rises like a cathedral on which generations have labored. It is never finished; the plans are altered, each generation adds its bit, and perhaps under the foundations are discovered the remains of earlier and more primitive designs. One is almost tempted to carry the figure farther and to speak of "styles" of the various eras. The lack of homogeneity of the material in Beilstein speaks most eloquently. It shows the intimate interlacing of research and daily life, and demonstrates, at the same time, the deep-seated change that one hundred fifty years of organic chemistry have wrought in the concepts underlying proofs of structure. The Kekulé theory is the fundament of the present edifice; it is truly amazing that though our ideas have been considerably refined, all the progress of modern science, including physical-chemical methods, has not undermined this foundation. However, the discerning reader will be conscious of many compounds in which traces of the inadequate methodology of the earlier periods can be detected and, untouched by modern developments, these have, to a certain extent, fallen by the wayside. Not only unimportant compounds have suffered this fate. It would be a mistake to consider this material dead; even in the most unfavorable cases it will have value as a part of the great storehouse of empirical experimental findings. Who can say how soon theoretical or technical needs will bring about a reawakened interest in materials that now lie neglected? Perhaps among these blocks discarded by the architect are future cornerstones.

An attempt has been made to give the reader a glimpse into the workshop of the Beilstein editorial staff. Chemists can be justly proud of this great accomplishment. It is a practical reference work, but for him who reads between the lines it also is a living demonstration of the never-ending progress and the limits of science.

COLLATERAL READINGS *in* INORGANIC CHEMISTRY*

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AUTHORS of texts in inorganic chemistry commonly recognize the desirability of references to corroborative and supplementary literature. This is evidenced by the frequency with which references to articles and books appear at the end of most chapters in texts on inorganic chemistry at both the college and the high-school level. As a matter of fact, some texts cite so many references that a student could spend a whole semester reading only the references at the end of a single chapter, though no such student has yet been discovered. However, in a number of cases blanket inquiries directed to whole classes of students in elementary organic chemistry who have been exposed to a year of high-school chemistry, as well as a year of college chemistry, failed to elicit the name of a single chemical journal or journal devoted largely to chemistry, or even a single eminent chemist—that is, a living one. The latter situation has been remedied to some extent during the past few years since two American chemists achieved the Nobel laureate and the front page. However, the average undergraduate is still quite unaware of any chemical journals, and obviously full use is not being made of the literature references so commonly encountered at the end of each chapter.

Nevertheless, examination of the authoritative journals published or sponsored by the American Chemical Society will reveal the existence of a truly surprising number of articles which are intelligible to the student who has had little or no chemistry. Recently two valuable papers by Professor Alyea[1] have appeared in the JOURNAL OF CHEMICAL EDUCATION, indicating a large number of articles suitable for freshman students which have been published in *Chemical and Metallurgical Engineering* and in the *Journal of Industrial and Engineering Chemistry*. Such articles may very profitably be incorporated in the formal course in inorganic chemistry. The modern text of elementary chemistry furnishes an extremely concentrated diet of factual data, as difficult for a student to assimilate as so much graphite and cellulose, and about as nourishing. Further, there seems to be an increasing tendency to concentrate on physical chemistry in the elementary inorganic chemistry course. The gaunt physical skeleton of the facts is far more pleasing when it is filled in and rounded out with details that are basically, perhaps, less essential but are, nevertheless, important to the broader development of the student. These details no text can give, for after all the text is built up by the extreme condensation or rectification of thousands of articles in the literature.

The desirability of extending text and lecture with corroborative and supplementary material from the original chemical literature is a matter of general agreement among teachers of chemistry. It is generally conceded that freshman chemistry is a professional course—it leads up to analytical chemistry and organic chemistry—and usually the better it is as a professional course, the worse it is as a cultural course. Properly selected articles not only serve to introduce the student to the chemical literature, but broaden his perspective of the field of chemistry. They supply breadth to the depth of the text. For the general student they provide a very necessary external source of inspiration, background information, and constantly recurring evidence that chemistry is a living vital force in the practical life of today. "The professional student will not be handicapped by the fact that he was permitted the opportunity to enjoy chemistry during his freshman year."

Last year the assignment of such articles as required collateral reading was undertaken by the writer with a small class in organic chemistry. While these visitations were received with varying degrees of enthusiasm, the student response was, on the whole, quite satisfactory. In answer to an inquiry at the end of the year none would admit that such assignments were wholly without value, and some went so far as to say that this constituted one of the more outstanding features of the course. On the basis of the results obtained, a group of such articles suitable for students in elementary organic chemistry was collected into one volume. This was reported on at the meeting of the American Chemical Society in Pittsburgh in September, 1936, and is now being used successfully.

This year the assignment of articles as a regular part of the student's work was extended to another small class in inorganic chemistry. One article of rather less than an hour's reading time was usually assigned each week. A report was required on each article, but the mechanics of reporting were simplified as much as possible. Each report was required to contain four items. These were: (1) the title, author, and reference in the form in which they would appear as a reprint from the *J. Am. Chem. Soc.;* (2) the reading time;

* Based upon a paper presented before the Division of Chemical Education at the ninety-third meeting of the A. C. S., Chapel Hill, North Carolina, April 13, 1937.

[1] ALYEA, J. CHEM. EDUC., **13**, 76–81, 540–4 (1936).

(3) a letter grade, A, B, C, or D, to indicate the verdict as to the quality or value of the article; and (4) comment. These comments, which were left entirely to the student's discretion, were extremely varied and frequently wholesomely frank. Some undertook abstracts, more or less brief; some extracted phrases or sentences which seemed to them particularly interesting or informative (and these too were frequently revealing); others chose to offer a critical review; in a few instances extended comment on social behavior, inspired by the article, was offered. Very few of the reports received have failed to include any comment whatsoever. Occasional questions concerning relevant portions of the assigned readings were commonly introduced into the weekly quizzes, and occasionally objective-type quizzes were given. The results obtained from these quizzes were surprisingly good, as a large number of perfect scores were registered.

The value of such collateral readings was amply demonstrated. In making the assignments it was emphasized that reading rather than memorization was the objective. Students were urged in so far as possible to understand the subject-matter and master the vocabulary but not to be excessively perturbed at failure to absorb completely and retain everything presented in the articles they read. The difficulty of inadequate vocabulary and background is a vexatious one, and assignments must be made quite carefully and only after full consideration of the present status of the student's knowledge. Articles must contain an absolute minimum of material which is not readily intelligible to the student and should be assigned with a view to contributing to the student's back-log of information, and not on the assumption that he already has this background. An attempt is made to have the student realize that by such extensive reading he will pick up a great deal of information more or less unconsciously. The thought is not that, simply by physical contact between student and journal, some mysterious osmosis will enable the knowledge to diffuse out of the concentrated journals into the dilute students. However, I am convinced that mere perusal will result in considerable diffusion. I wish to quote a paragraph from a recent article by Professor Gomberg of the University of Michigan. "Early in my undergraduate course I undertook to go through the various sets of chemical periodicals, in English, that our library then contained. Page by page I read the first eleven volumes of each, the *American Chemical Journal* and the *Journal of the American Chemical Society*. The ramifications of your science did not appall me at that time as they do now. Articles in our journals on the composition of elephant's milk, or on the atomic weight of copper, or on tautomerism were all read through. Of course, a great deal of what I then read was above my head, but still it gave me a sense of acquaintance with the then prominent personalities and a desultory knowledge of the chemical problems of the day. . . .The writer may thus truly say that his chemical outlook has been engendered largely by his close acquaintance with the initial dozen slender volumes of the *Am. Chem. J.* and the *J. Am. Chem. Soc.*" I must confess that I have not read the first eleven volumes page by page, and doubtless it is that failure to which I must regretfully ascribe my own very much narrower outlook upon chemistry.

In reporting on articles students are only too likely to recall those incidents with which they had difficulty, and ignore the material which caused them no such embarrassment. As little as one or two paragraphs of unintelligible material in a five-page article will cause the whole article to be condemned by the demoralized student. The appearance of a single exponential equation in an otherwise intelligible article will demoralize the average student (though he has had algebra), while the introduction of a differential will paralyze any further intelligent perusal, and such an article will usually be condemned unhesitatingly as being entirely beyond his depth or over his head.

Such articles should not be "dragged in" simply because they happen to be interesting to the instructor. They must be properly integrated and contribute to the central theme—the important theories and principles, the descriptive facts and their industrial applications and economic aspects interlaced with suitable biographical and historical material. Articles need not be rejected simply because they are somewhat difficult. There is no illusion that this is light and airy reading which all comers can peruse with unalloyed pleasure. As with the stated Editorial Policy of the JOURNAL OF CHEMICAL EDUCATION, "Not every article can be expected to appeal to every reader. In a group of individuals whose immediate problems and interests vary so widely such a condition is inevitable. The happy equilibrium to aspire to is that some articles will appeal to everyone and all articles appeal to someone. Some, which though individually of limited appeal, will collectively through their diversity serve all the group." It is necessary to strike a balance between articles which are essentially theoretical, industrial, and historical in nature. The amount of abuse which the average liberal arts student freshman will tolerate from his science instructor without open rebellion is truly surprising. However, he will tend to resent the introduction of an excessive amount of material which is essentially industrial or engineering chemistry in nature. He will similarly resent an excess of the purely historical type of material as it seems to him that this simply adds to the burden of an already overladen course. Articles, even though properly integrated, should preferably not be assigned as just so much additional work. There is a world of difference between, "Just a few months ago Anderson won a Nobel Prize for the discovery of the positron two years ago, but just last year Darrow published an article on the discovery and early history of the positron which I should like you to read" and "Read an article by Darrow in the May issue of the *Scientific Monthly* with Chapter X of your text."

The chief difficulty, and probably the prime reason for the relatively few extra-textual assignments, is

TABLE OF CONTENTS

1. The Human Side of Chemistry. Edwin E. Slosson, *Ind. Eng. Chem.*, **14**, 887–93 (1922).
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Appendix

encountered in the attempt to secure adequate numbers of the requisite journals. Smaller institutions simply do not subscribe to such journals, and larger institutions do not have a sufficient number of copies for their correspondingly larger numbers of students. The problem was at first solved temporarily by using borrowed journals. On the whole, the students suffered less than the journals, and this developed into an excellent technic for determining student interest. The relation of student interest to journal depreciation was simple and direct. This year in our classes in organic chemistry individual copies of a single volume containing a collection of articles reproduced from current journals are being used successfully.

It is recognized that such a collection has the disadvantage of not giving the students direct access to the journals proper. On the other hand, this method of presentation has several advantages from a pedagogical point of view. Thus collateral readings may be much more readily integrated with the other features of the course. An opportunity is provided to include the small amount of introductory or explanatory material which will frequently clarify any minor but, nevertheless, annoying difficulties a student may encounter. A wider range of selection is permitted, since the more difficult or less pertinent portions of an article may be omitted if it is not desirable to reproduce all the articles in their entirety. Several related articles appearing at different times, possibly in different journals, may be grouped together, giving a more unified picture to the student who has not yet learned readily to correlate the content of different articles. A very definite advantage is that the student has the volume at home at his own desk where it is available at all times for leisure reading, and he will not have to go to the library for this material. We all know from our own experience that we are much more likely to read our chemical journals regularly when they arrive at our desk than when we depend upon a library copy, since unfortunately we are not all Gombergs.

It is planned for next year to produce a similar collection for inorganic chemistry.* The table gives a list of articles considered for inclusion, and it is this list particularly that I should like to form the basis for discussion. I should very much appreciate suggestions as to additions, deletions, or substitutions—as unquestionably the reader is familiar with individual articles which he would very much want his own students to read if there were only some easy way of making them readily available.

* *Editor's Note:* The projected collection has since appeared. For review see J. CHEM. EDUC., **15**, 247–8 (1938).

An EXPERIMENT ILLUSTRATING *the* RELATION *between* E.M.F. *and the* EQUILIBRIUM CONSTANT

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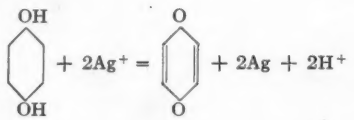
ALTHOUGH nearly every laboratory manual of physical chemistry (which is written in English) includes an experiment illustrating the use of E.M.F. measurements in the determination of concentration differences, to the best of our knowledge, only two (*1, 2*) include an experiment on the equally important relation between E.M.F. and the equilibrium constant (or standard free energy) of an oxidation-reduction reaction. Both of these use the following reaction as an example

$$Fe^{+++} + Ag = Fe^{++} + Ag^{+}$$

Unfortunately, this reaction involves both experimental and theoretical difficulties. The reaction system must be carefully protected from air; the measurement of the cell as described (*1, 2*) is rendered uncertain by an unknown and probably large liquid junction potential; and the activity factor, $\gamma_{Ag^+}\gamma_{Fe^{++}}/\gamma_{Fe^{+++}}$, is neither negligible nor subject to independent measurement.

These several difficulties can be minimized by the use of the following reaction, which possesses some intrinsic interest because of its relation to photographic development.



It has been shown experimentally, that the action of air on this system is negligibly slow. The cell can be conveniently designed to practically eliminate the liquid junction potential. For measurements in dilute solution, no appreciable error is introduced by assuming that the activity factor, $\gamma_{Ag^+}/\gamma_{H^+}$, is equal to unity.

A classroom experiment, based upon the technic described in the following parts of this paper, was performed by approximately one hundred students in the last year, and proved to be satisfactory. The technic is neither difficult nor laborious, and the results are sufficiently accurate to encourage the student. In the direct or analytical determination of the equilibrium constant, equilibrium may be approached from either direction, although it is more convenient to start with hydroquinone and silver nitrate. The approach to equilibrium can be readily demonstrated by withdrawing and analyzing samples at regular intervals. Since the cell attains equilibrium very rapidly, a determination of its temperature coefficient and a computation of the heat of reaction may be included in the experiment.

ELECTROMOTIVE FORCE METHOD

This method involves the measurement of the E.M.F. of the cell, Pt | Quinhydrone (S), HNO_3 (0.1 *M*) | HNO_3 (0.1 *M*), | HNO_3 (0.1 *M*), $AgNO_3$ (0.001 *M*) | Ag. Since the concentration of nitric acid is the same in both half-cells and the concentration of silver nitrate in the silver half-cell is relatively small, the liquid junction potential is negligibly small.

The cell may be constructed from two half-cell vessels of the ordinary simple type, connected electrolytically by having their side tubes dipping into a small vessel containing nitric acid of the same concentration as in the cell. A 2-liter beaker filled with water, with manual stirring and temperature regulation, constitutes a simple and satisfactory thermostat.

Silver electrodes may be prepared by plating platinum wire electrodes with silver from a slightly acid five per cent. silver nitrate solution, using a second platinum wire as anode, and a single dry-cell battery (1.5 volts) as source of current with a plating time of five to ten minutes. Electrodes prepared in this way are satisfactory and reproducible. A plain platinum elec-

TABLE 1

THE ELECTROMOTIVE FORCE OF THE CELL

Pt | Quinhydrone, HNO_3 (0.1227 *N*) | HNO_3 (0.1227 *N*), $AgNO_3$ (0.00100 *N*) | Ag at Various Temperatures, and the Equilibrium Constant, Standard Free Energy Change, Standard Change in Entropy, and Standard Heat of the Reaction

$$2Ag^+ + H_2Q \rightleftarrows 2Ag(S) + Q + 2H^+$$

t°C.	Time	$E_{obs.}$ v.	$K_{obs.}$ × 10^{-3}	$-\Delta F°_{obs.}$ cal.	$-\Delta H°_{obs.}$ cal.	$\Delta S°$ cal. deg.$^{-1}$
19.23	10	−0.01950				
	30	−0.01946	3.21	4688	13320	29.53
25.00	..	−0.02317[a]	2.48	4629	13450	29.59
25.42	10	−0.02348				
	20	−0.02348				
	30	−0.02344	2.43	4624	13450	29.57
31.38	10	−0.02728				
	20	−0.02732				
	30	−0.02730				
	60	−0.02726	1.89	4565	13580	29.61

[a] Interpolated value.

$\frac{dE}{dT}$ = −0.000642 volt/deg. between 19° and 32°C.

trode is used in the quinhydrone half-cell, which contains an excess of solid quinhydrone.

In order to determine the temperature coefficient of cells of this type, and the time necessary to reach equilibrium after a change in temperature, the measurements recorded in Table 1 were performed. For these measurements the cell was kept in a thermostat whose temperature could be maintained constant to ±0.02°C., and a potentiometer system was used with which readings could be made to ±0.01 MV. The measurements were made without excluding air from the cell. The silver electrode was negative to the quinhydrone electrode.

These data show that the cell attains constant E.M.F. very quickly after a change in temperature. The temperature coefficient is quite large, and is linear between 19° and 32°C.

The E.M.F. of the cell, neglecting the (very small) liquid junction potential, is given by the thermodynamic expression,

$$E = \frac{RT}{2F_y} \ln K - \frac{RT}{2F_y} \ln \frac{C^2_{H^+}\ \gamma^2_{H^+}\ C_Q\gamma_Q}{C^2_{Ag^+}\ \gamma^2_{Ag^+}\ C_{H_2Q}\gamma_{H_2Q}} \qquad (1)$$

in which,

$$K = \left[\frac{C^2_{H^+}\ \gamma^2_{H^+}\ C_Q\gamma_Q}{C^2_{Ag^+}\ \gamma^2_{Ag^+}\ C_{H_2Q}\gamma_{H_2Q}}\right]_{equil.} \qquad (2)$$

In these equations the symbols H_2Q and Q refer to hydroquinone and quinone respectively, and γ is the activity coefficient.

We also have the relations,

$$\frac{RT}{2F_y} \ln K = E^\circ_{Ag^+,\,Ag} - E^\circ_{QH} = E^\circ_{cell} \qquad (3)$$

in which $E^\circ_{Ag^+,\,Ag}$ and E°_{QH} are the standard potentials of the silver and quinhydrone electrodes.

Since the silver and hydrogen ions are univalent, and since the ionic strengths in the two half-cells are small and very nearly equal, it may be assumed without appreciable error that $\gamma_{Ag^+} = \gamma_{H^+}$. Furthermore, in the quinhydrone half-cell $C_{H_2Q} = C_Q$, and at an ionic strength of 0.1 we may safely assume that $\gamma_{H_2Q} = \gamma_Q$. These simplifying assumptions have been used in the computation of the values of $K_{obs.}$, and the related thermodynamic quantities given in Table 1.

At 25°C. the standard potentials of the silver and quinhydrone electrodes are 0.7996 v.[3] and 0.6994 v.[4], respectively. Substituting these values into Eq. (3) we obtain a value of 2.45×10^3 for K at 25°C. Using this value of K and the temperature coefficient given in Table 1, we find for the reaction

$$2Ag^+ + H_2Q \rightleftarrows 2Ag\ (S) + Q + 2H^+,$$

$$\Delta F^\circ_{298} = -2.303\ RT \log K = -4624 \text{ cal.} \qquad (4)$$

$$\Delta H^\circ_{298} = \Delta F^\circ_{298} + 2F_yT\left(\frac{dE}{dT}\right) = -13{,}452 \text{ cal.} \qquad (5)$$

These may be regarded as the accepted values at 25°C., with which we may compare the observed values given in Table 1. The difference between the observed and the accepted value of K at 25°C. corresponds to an error of only 0.18 MV. in the measured E.M.F. of the cell. It appears, therefore, that the assumptions we have made regarding the equality of the activity coefficients of the hydrogen and silver ions and the neglect of the liquid junction potential are justifiable.

This cell has the following didactic advantages: (1) the cell is readily assembled from simple apparatus, and the measurements can be made in the presence of air; (2) the temperature coefficient is quite large and practically linear between 19° and 32°C., so that it may be determined with satisfactory accuracy using "student technic"; (3) the cell reaches constant E.M.F. very quickly after a change in temperature; (4) the thermodynamic quantities K, ΔF°, ΔH°, and ΔS° can be accurately determined from the measurements because no uncertain assumptions regarding activity coefficients are involved, and the liquid junction potential is negligibly small.

ANALYTICAL METHOD

This method involves the preparation of a reaction mixture containing known initial concentrations of hydroquinone, nitric acid (or perchloric acid), and silver nitrate, if the equilibrium is to be approached from the hydroquinone side, or a mixture containing finely divided silver and known concentrations of quinone and nitric acid if the equilibrium is to be reached from the quinone side. Since the initial concentrations are known it is only necessary to analyze for one component.

Preliminary work demonstrated that it is most convenient to analyze the reaction mixtures for quinone by iodometric titration according to the method of Valeur (*5*, *6*). This method is based upon the reduction of quinone by iodide ion in strongly acid solution with the liberation of an equivalent amount of iodine which is titrated with thiosulfate.

The technic of the experiments is best explained by describing a typical experiment. In this experiment 0.8250 g. of hydroquinone was weighed into a clean dry gas-washing bottle and dissolved in 75 cc. of water which was added from a pipet. One hundred fifty cc. of 0.2010 *N* perchloric acid and 75 cc. of 0.1000 *N* silver nitrate were then added by pipetting in the order named. The bottle was placed in a water thermostat at 25°C., and a stream of nitrogen was bubbled through the solution for stirring. The initial mixture thus had the composition $HClO_4$ 0.1005 *M*, $AgNO_3$ 0.025 *M*, and hydroquinone 0.025 *M*.

After various intervals of time 10-cc. samples of the reaction mixture were removed with a pipet and analyzed for quinone as follows. The 10-cc. sample was delivered into 10 cc. of ten per cent. potassium iodide solution in a 250-cc. Erlenmeyer flask, which caused the complete precipitation of the silver as silver iodide and the reduction of the quinone to hydroquinone with the liberation of an equivalent amount of iodine. From 5 to 10 cc. of 6 *N* hydrochloric acid were then added to insure complete reduction of the quinone, and after addition of 3 cc. of 0.2 per cent. starch solution the liberated iodine was titrated with 0.01 *N* thiosulfate.

Special experiments showed that the presence of the precipitated silver iodide had no effect on the accuracy of the titration. Its only effect was to obscure the starch endpoint slightly, but this effect is not serious and the endpoint is readily detectable to ± 0.05 cc. of 0.01 N thiosulfate. It was found that the titration is accurate to about ± 0.2 per cent.

A blank titration using the same amounts of the reagents as used in a titration should be run in order to correct for the small amount of iodine that is usually present in the potassium iodide solution. In our experiments this blank correction varied between 0.1 and 0.3 cc. The titration should be made immediately after taking the sample, in order to avoid air oxidation of the iodide in the strongly acid solution. For the same reason the additional acid should be added after the sample and just before starting the titration.

The complete data of the foregoing experiment are given in Table 2.

TABLE 2

DATA OF A TYPICAL EXPERIMENT

Temp. = 25°C.

Time, Min.	0.00996 N $Na_2S_2O_3$ cc. (corrected)	Concentrations—moles per liter $HClO_4$	$AgNO_3$	H_2Q	Q
0	—	0.1005	0.0250	0.0250	0
22	0.4				
33	4.6				
41	18.9				
50	21.60				
64	22.31				
99	22.55				
144	22.52	0.1229	0.0026	0.0138	0.0112

$$K = \frac{(0.1229)^2(0.0112)}{(0.0026)^2(0.0138)} = 1.8 \times 10^1$$

It will be noted from the data of Table 2 that during the first twenty minutes the speed of the reaction was very small, and that the rate increased rapidly after this time. This initial slow rate corresponds to an induction period which was characteristic of those experiments where no metallic silver was present originally.* Under these conditions, the solution remains clear for ten or fifteen minutes, after which time silver starts to precipitate in a finely divided form and the solution gradually becomes turbid. The reaction does not accelerate immediately after the first appearance of silver; usually ten or fifteen minutes more are required before the rate increases. During the further course of the reaction the finely divided silver agglomerates into a compact mass and the solution becomes clear.

The results of three experiments which illustrate the effect of the initial concentrations on the reaction velocity are plotted in Figure 1. It is evident from these results that a low concentration of acid favors rapid attainment of equilibrium. Unfortunately, if the acid concentration is appreciably less than 0.10 N the reaction goes so near to completion that it is impossible to determine the equilibrium concentrations with any accuracy. The optimum concentration of acid appears to be between 0.10 and 0.15 N.

To further investigate the induction period and the effect of having metallic silver present at the start of the reaction, five experiments were performed using the same initial concentrations of hydroquinone (0.0250 M), silver nitrate (0.0250 M), and nitric acid (0.106 M).

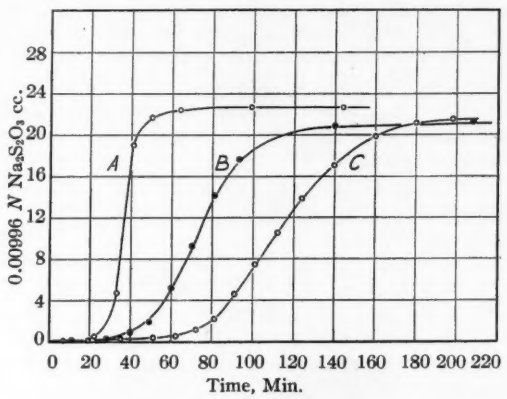


FIGURE 1.—INFLUENCE OF ACID CONCENTRATION ON REACTION RATE

A (No. 2, Table 3.) 0.100 N HNO_3, 0.025 M $AgNO_3$, and 0.025 M hydroquinone.

B (No. 7, Table 3.) 0.182 N HNO_3, 0.025 M $AgNO_3$, and 0.025 M hydroquinone.

C (No. 8, Table 3.) 0.328 N HNO_3, 0.0300 M $AgNO_3$, and 0.0200 M hydroquinone.

No silver was present at the start of these experiments.

The reactions were carried out in carefully cleaned 500-ml. Kjeldahl flasks, which were all shaken under identical conditions in a water thermostat at 25° in the presence of air. One flask was paraffined, another was left plain, and to the three remaining, 1 g., 3 g., and 10 g., respectively, of finely divided silver were added. The silver was treated with dilute nitric acid and washed thoroughly with distilled water just before it was used. The results of these experiments are shown diagrammatically by the curves in Figure 2.

These curves show that there was no marked difference in the rate of the reaction in the paraffined and the plain flasks; a definite induction period of forty to sixty minutes was found in both experiments, and from the trend of the curves it is evident that more than four hours was required to reach equilibrium. After twenty-four hours' shaking, equilibrium had been reached in both cases.

In the presence of the finely divided silver there was no induction period, as shown by curves (3), (4), and (5), but the reaction started as soon as the reactants were mixed together and proceeded at a steady rate, and equilibrium was attained in two to three hours.

When the reaction mixtures are shaken for too long a time after equilibrium has been reached, the solutions

* These results suggest that the induction period is caused by slow crystallization or agglomeration of the metallic silver, which is accelerated by the added silver.

acquire a reddish color and the quinone titre decreases, probably due to slow side reactions involving the de-

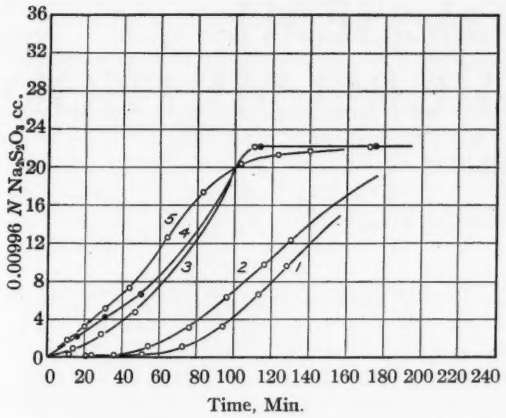


FIGURE 2.—ACCELERATION OF THE REACTION $2Ag^+ + H_2Q \rightarrow 2Ag(S) + Q + 2H^+$ BY METALLIC SILVER. INITIAL CONCENTRATIONS IN ALL EXPERIMENTS WERE: HYDROQUINONE 0.025 *M*, SILVER NITRATE 0.025 *M*, AND NITRIC ACID 0.106 *M*; SHAKEN IN 500 CC. KJELDAHL FLASKS AT 25°C.

(1) Plain flask, no silver.
(2) Paraffined flask, no silver.
(3) 1 g. silver present.
(4) 3 g. silver present.
(5) 10 g. silver present.

composition of quinone. (Solutions of pure quinone exhibit the same color changes on long standing.) In a typical experiment, equilibrium was reached after three hours, at which time the quinone titre was 23.28 cc. of 0.00996 *N* thiosulfate corresponding to a value of *K* of 4.3×10^3. After shaking for twenty-eight hours the titre decreased to 22.88 cc. and after five days to 21.03 cc. It is evident, therefore, that the experiments should not be prolonged for more than a few hours after equilibrium has been reached.

TABLE 3

SUMMARY OF RESULTS BY THE ANALYTICAL METHOD

Temp. = 25°C.

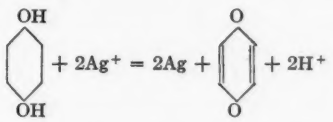
	Initial Concentrations				*Equilibrium Concentrations*				
No.	*Acid* *M.*	H_2Q *M.*	$AgNO_3$ *M.*	*Q* *M.*	*Acid* *M.*	H_2Q *M.*	$AgNO_3$ *M.*	*Q* *M.*	*K* $\times 10^{-3}$
1	0.1005	0.0250	0.0250	0	0.123	0.0138	0.0026	0.0112	1.8
2	0.1005	0.0250	0.0250	0	0.123	0.0137	0.0024	0.0113	2.3
3	0.1005	0.0250	0.0250	0	0.123	0.0138	0.0026	0.0112	1.8
4	0.0957	0.0250	0.0250	0	0.119	0.0134	0.0017	0.0117	4.3
5	0.1061	0.0250	0.0250	0	0.128	0.0139	0.0028	0.0111	1.7
6	0.1061	0.0250	0.0250	0	0.128	0.0139	0.0028	0.0111	1.7
7	0.182	0.0250	0.0250	0	0.202	0.0148	0.0046	0.0102	1.3
8	0.328	0.0200	0.0300	0	0.350	0.0092	0.0084	0.0108	2.1
9	0.201	0	0	0.0229	0.211	0.0050	0.0100	0.0179	1.6

A summary of some results obtained by the analytical method is given in Table 3. In the first eight experiments equilibrium was approached from the hydroquinone side, and in the last experiment from the quinone side.

As is to be expected, the results are not as precise nor as accurate as those obtained by the E.M.F. method, but are entirely satisfactory for this type of method.

SUMMARY

1. The reaction



serves excellently to illustrate the relation between E.M.F. and such thermodynamic quantities as *K*, ΔF°, and ΔH°.

2. The cell

Pt|Quinhydrone(S) HNO_3 (0.1 *M*) HNO_3 (0.1 *M*) HNO_3 (0.1 *M*), $AgNO_3$ (0.001 *M*) Ag

is easily constructed, is not appreciably affected by air, and attains its equilibrium value almost immediately. The values of *K*, ΔF° and ΔH° based upon measurements of such a cell are in excellent agreement with the standard values.

3. The equilibrium constant may be measured directly by analyzing a reaction mixture of known initial concentration for quinone content. Since the reacting mixture is not sensitive to air, the progress of the reaction may be followed conveniently by withdrawing samples from time to time. With a suitable choice of initial concentrations, with proper stirring, and in the presence of a few grams of finely divided silver (to act as catalyst), equilibrium is reached in about two hours. Since quinone undergoes a slow decomposition in solution, the reaction mixture should not be allowed to stand for more than ten or fifteen hours before the final titration. Because of this side reaction, the measurements do not yield as accurate results when the equilibrium is approached from the quinone side, although the equilibrium constant is still of the right order of magnitude.

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The TEACHING *of* QUALITATIVE ANALYSIS *by the* SEMI-MICRO METHOD*

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THE adaptation of methods of microanalysis to the ordinary procedures of qualitative analysis for elementary instruction was first described by Engelder and Schiller of the University of Pittsburgh in 1932.[1] Certain advantages of this type of course over the usual one were pointed out by these men.

The author gave a course in semimicro qualitative analysis in the first semester of the past academic year in place of the macro system. The recent textbook by Engelder, Dunkelberger, and Schiller was used.[2] A class of twenty second-year chemistry students completed the semester's work, and the following report is the result of an analysis of the facts learned from first-hand experience with the course. Some of these facts were gleaned from the answers to a questionnaire given to the students at the end of the semester in order to obtain the valuable and constructive criticism of those who had taken the course. Other facts are the results of a statistical analysis and comparison of results obtained in this course and in the macro courses given by the author during the preceding four years.

The students without exception stated that they preferred the semimicroanalysis to the introductory qualitative analysis study with which they had been acquainted in their general chemistry course, and which was of the conventional type. Many of them remarked that they felt they were pioneering in a new field, and that this fact increased their interest. A few stated they had at first felt that they were going to be cheated out of a good course in qualitative analysis by the employment of this new method, but that they soon became enthusiastic about it and realized they were really doing something very much worth while. This viewpoint is in itself a distinct advantage of the semimicro method. New blood and new life in the qualitative analysis course will certainly aid in preventing it from becoming a mere routine of instruction, and this new technic will keep both teachers and students alert and interested in the work and its advancement.

Students in this class were encouraged to use their initiative and inventive powers in planning the best ways to perform the experiments. They soon discovered that it was a decided advantage to have one's reagents and apparatus arranged in some definite order, and several original schemes of arrangement were evolved, such as the use of small boxes for storage of equipment, and the use of various homemade racks, some quite cleverly constructed, for pipets and centrifuge tubes. In short, ingenious students were given ample opportunity to use their talents, and the response of these students was most gratifying.

It is the author's conviction, based upon observation, that the semimicro course has several distinct advantages over the macro system, both for the instructor and for the student. One of the objects of a good analytical course is to teach neatness and care in manipulation. Working with small quantities of material, one drop to one ml. in magnitude, precludes the use of careless or slipshod methods. The tests, if properly made, are as easily detected as when larger quantities are employed, but small amounts of contaminating materials are particularly significant in small samples.

Teaching of chemical principles and reactions may be achieved very effectively in the semimicro course, for the systematic separations are practically identical with those of the older type of course. Fractional precipitation with hydrogen sulfide in solutions of adjusted pH, for example, is the same for either course. In addition, an acquaintance with modern organic reagents and the modern spot test technic is obtained. In brief, there need be no sacrifice of thorough training in fundamental principles. Rather, this is enhanced, since a greater variety of reactions and methods are available.

The semimicro course has a practical aspect which students especially appreciate. Frequently in commercial or practical analyses only small quantities of samples are obtainable, and in such cases the ordinary macro-analysis is of little use. Micro-analytical methods were originated to overcome this difficulty, and the semimicro course greatly increases the scope of the analyst's training, enabling him to handle very small samples when necessary.

In our course, the students were required to estimate the amounts of each ion present in their unknown sam-

* Presented as part of the Symposium on the Teaching of Qualitative Analysis, Midwest Regional Meeting of the A. C. S., Omaha, Nebraska, May 1, 1937.

[1] ENGELDER, C. J. AND W. SCHILLER, "A system of qualitative microanalysis," J. CHEM. EDUC., **9**, 1636 (Sept., 1932).

[2] ENGELDER, C. J., T. H. DUNKELBERGER, AND W. J. SCHILLER, "Semi-micro qualitative analysis," John Wiley & Sons, Inc., New York City, **1936**.

ples. Their known samples for practice analysis contained what we arbitrarily called a "medium" amount of each ion, namely, 1.0 mg. per ml. The "large" and "small" amounts were 3.0 and 0.5 mg. per ml., respectively. A fair degree of accuracy in estimating the relative quantities of the ions present was attained by the students. Although the concentrations of ions in the samples were only about one-third as great as those which the author had used in previous courses in qualitative analysis, the results compared quite favorably with earlier work using the macro-analysis. The concentrations given above, however, are not proposed as ideal values. Probably an improvement in instructional value of the unknown samples will be accomplished by doubling these quantities. The purpose is to give samples with which a fairly high degree of accuracy may be obtained by students, yet not so easy that careless or questionable methods may be employed with expectation of good results.

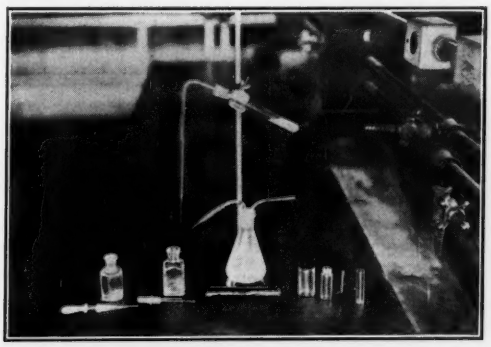


FIGURE 1.—TYPES OF REAGENT BOTTLES USED. WASH BOTTLE. H_2S GENERATOR

From the standpoint of the instructor, the ease of preparation of unknown solutions for analysis is worthy of note. A complete set of stock solutions of ions was made up. These contained ten mg. of the ion in one ml. of solution, and were kept in 30-ml. dropping bottles of the Barnes type. Since one drop contained approximately 0.5 mg., an unknown sample was prepared readily by simply taking the required number of drops of each stock solution, mixing, and diluting to the correct final volume. Thus two, four, and nine drops of stock solution represented small, medium, and large concentrations, respectively, in a total volume of 2 ml. Of the 2-ml. sample, the student took 1 ml. for analysis, and reserved the remainder for use only in case of necessity. This system for dispensing unknowns was so simple that about two minutes were sufficient for preparing a sample, since no cleaning and rinsing of pipets or graduates was necessary. No two unknowns were of the same composition, and only about five ml. or less of the stock solution of each ion were used up in the semester's work for preparing unknown solutions for the class of over twenty students. The students prepared samples of known composition from a similar set of stock solutions kept in the laboratory, and used these solutions for practice. In addition, various alloys and solid salt mixtures were dispensed in small amounts for some of the final analyses.

Not the least of the advantages of the semimicro course from both students' and instructor's viewpoint is the use of individual sets of reagents. The student was given a complete set of vials and small reagent bottles of various types, which he filled with the proper reagents from stock bottles as his needs for them arose (Figure 1). The acids and alkalies were kept in 30-ml. bottles equipped with droppers. Solids were kept in small cork-stoppered "shell" vials of about 3 ml. capacity. About 2 ml. of the special liquid reagents which were to be used in amounts of one or two drops at a time were put in screw-capped vials with applicators. Other liquid reagents which were to be used in larger amounts or very frequently were placed in screw-capped vials of about 10 ml. capacity. It is very desirable to use a bottle of this capacity equipped with a dropper, for the students found that a considerable amount of time was consumed keeping extra pipets and droppers clean for use with these reagents.

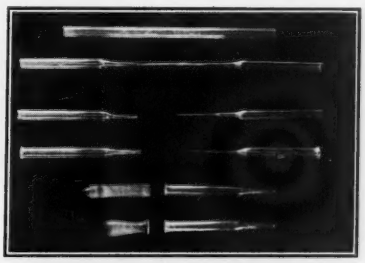


FIGURE 2.—STEPS IN THE MAKING OF DROPPERS (*left*) AND CAPILLARY PIPETS (*right*). THE BULB MAY BE MADE OF 1/4 INCH TUBING AS SHOWN, IF DESIRED

The use of individual reagents minimizes the undesirable congestion about reagent shelves, and their use also fixes the responsibility for care of the reagents upon each student in the course. The contamination problem is an individual one, and only one student suffers when he allows his reagents to become impure through carelessness. Some students may be a bit skeptical of the need for cleanliness at first, but a little experience and observation soon brings them to their senses. Furthermore, the use of individual reagents permits the student to do most of his work in comfort, sitting on a stool at his own desk, and tending strictly to his own business. It was found that nearly every student in the course took a just pride in arranging his equipment so that his workbench space became his

own little laboratory, practically complete in every detail.

The outsider entering the ordinary qualitative analysis laboratory is greeted by the odor of hydrogen sulfide, and carries the resulting impression with him forever after. The laboratory in which semimicro analysis is taught is surprisingly free of this and other objectionable gases and fumes, such as NO_2, SO_2, HCN, Cl_2, and others. The small quantities of materials used in the tests almost eliminate these customary laboratory smells. In our course, we prepared hydrogen sulfide by heating a mixture of sulfur, paraffin, and asbestos in

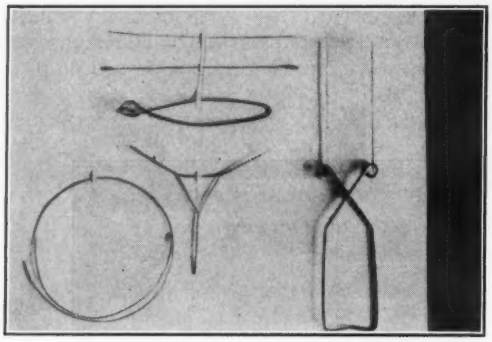


FIGURE 3.—SHOWING STEPS IN MAKING NI WIRE SPATULA (*top*); NICHROME WIRE TRIANGLE (*lower left and center*); TEST-TUBE HOLDER (*center*). SLIDE-HOLDER AND ORDINARY MICROSCOPE SLIDE (*right*) SHOW RELATIVE SIZES

individual generators consisting of test-tubes fitted with capillary delivery tubes and mounted on ring-stands (Figure 1). Although, as a rule, the generator was used at the student's desk and not in the fume hood, little hydrogen sulfide odor was created, and very much less than ever before in the author's experience with the ordinary course, even with the best of hydrogen sulfide systems and fume hoods.

From an economic viewpoint, the advantage is almost entirely with the semimicro method of instruction. Obviously, only a small fraction of the usual amounts of reagents and chemicals are used. In addition, only a small amount of reagent is readily available in the student's reagent bottle, and since it must be dispensed with a dropper or applicator, waste is reduced to a minimum. There is also a considerable saving of the time required in preparing solutions of reagents for a laboratory class, for it was found that one 100-ml. portion of each solution was generally sufficient to last the whole class throughout the entire semester.

Another economic advantage is the moderate cost of apparatus used in the semimicro course. For the most part, it is simple and inexpensive. Prices on some pieces, however, are much higher than seems justified. For example, the small centrifuge tubes of Pyrex glass seem unduly expensive. However, they can be made at very little cost by anyone with a most elementary knowledge of glassblowing. Our students made many of their own centrifuge tubes, and thus profited both financially and educationally by the experience. Micro crucibles cost more than the regular sizes, but there was very little breakage of these articles, and thus very little expense to the students on this account. Although it might seem that the cost of the many sets of

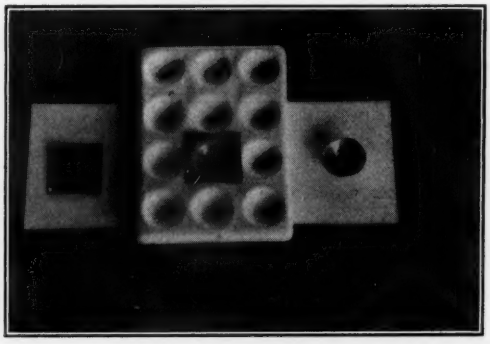


FIGURE 4.—MAKING LEAD DISH. 4-CM. SQUARE OF THIN SHEET LEAD MOLDED IN SPOT TEST PLATE; TRIMMED WITH SHEARS

individual reagent bottles would be large, it is not unduly high, since most of the bottles are of inexpensive types. Much of the apparatus can be made quite easily. Racks or blocks for reagent bottles and centrifuge cones may be constructed cheaply by the school carpenter or anyone handy with tools. In our course, several articles of equipment were made by the students as part of their laboratory work. These include hydrogen sulfide generators and wash bottles (Figure 1), medicine droppers and capillary pipets (Figure 2), nichrome wire triangles, test-tube holders of spring brass wire, nickel wire spatulas (Figure 3), lead dishes for the fluoride test (Figure 4), and even some centrifuge tubes (Figure 5).

Electric centrifuges were constructed by the author at a cost of about $6.00 apiece for materials (Figure 6). They were controlled by rheostats, which were also constructed at negligible cost. The motors were rebuilt Hamilton-Beach sewing machine motors, and were purchased for $5.00 each. These were mounted firmly on a heavy wooden base. The head was made of brass. At least one centrifuge for each six or eight students is desirable, and it should be inclosed in a sheet metal box to prevent accidents.

Comparison of the actual breakage charges of the students in the semimicro course and students in two earlier classes in macro-analysis courses shows that the expense to the student is much less in the former. In fact, the smallest breakage charge in the two macro qualitative analysis courses was larger than the average charge in the semimicro course. In the former, the

average charge per student was $5.74, while in the latter it was only $3.58.

A comparison of the analytical results obtained in the present course and those obtained in five earlier classes in which the ordinary system of qualitative analysis was used is shown in the accompanying tables. Complete records on all samples issued in two of these previous macro courses were available. The results in the tests for cations alone are given (Table 1). In this summary are listed the number of times each cation was potentially present in the unknown samples issued, the number of times it was correctly reported present or absent, as the case might be, and the percentage of correct reports out of the total number of times tested.

TABLE 1

COMPARISON OF RESULTS OF ANALYSIS OF CATIONS. (TWO CLASSES, MACRO; ONE CLASS, SEMIMICRO)

Ion	*Times tested (Macro)*	*Times reported correctly*	*Per cents.*		*Times reported correctly*	*Times tested (S-M)*
Ag	17	17	100	94	47	50
Hg^{+}	17	17	100	92	46	50
Pb	28	20	71	86	43	50
Bi	28	22	79	84	42	50
Cu	28	25	89	94	47	50
Cd	28	24	86	72	36	50
Hg^{++}	28	22	79	74	37	50
As	28	25	89	80	40	50
Sb	28	22	79	82	41	50
Sn	28	20	71	86	43	50
Al	34	33	97	88	44	50
Zn	34	32	94	62	31	50
Cr	34	33	97	90	45	50
Fe	34	29	85	90	45	50
Mn	34	30	88	92	46	50
Ni	34	34	100	88	44	50
Co	34	31	91	72	36	50
Ba	35	30	86	96	48	49
Sr	35	32	91	78	39	49
Ca	35	31	89	84	42	49
Mg	35	34	97	92	46	49
NH_4	35	33	94	78	39	49
Na	35	28	80	78	39	49
K	35	32	91	74	37	49

It is evident that in several cases the tests used in the semimicro class were apparently less reliable than those used in the conventional type courses taught by the same instructor. Some of these seeming weaknesses of the semimicro method were either reduced or quite completely eliminated by various means during the progress of the course, and these cases will be discussed in more detail. It should be noted, too, that the concentrations of ions in the samples used in the semimicro course were somewhat smaller than those used in the other courses, and this would account for some of the apparent advantage of the macro tests. Note that the weak points of the semimicro tests appear from the table to be in the cases of the ions of Cd, Zn, Co, Sr, Hg (mercuric), NH_4, Na, and K.

The low percentage of correct results for the cadmium ion was probably due largely to faulty technic in adjusting the acidity of the solution in preparation for precipitating Group II cations with H_2S. The directions given in the text are inadequate, and students can scarcely be expected to obtain correct results when they are simply directed to "make the solution acid to methyl orange paper by carefully adding concentrated HCl from a capillary pipet." Usually the endpoint is overstepped so that the solution is much too acid, and Pb and Cd are not precipitated with Group II ions. Since the student had two chances to find lead, in Group I and again in Group II, the percentages for Pb detection did not fall as low as those for Cd. A method of adjusting the acidity of the solution to the correct value before precipitation of Group II was worked out and given to the students, with immediate improvement in results. This procedure is a modification of one used in micro-analysis, and is outlined briefly in the following diagram.

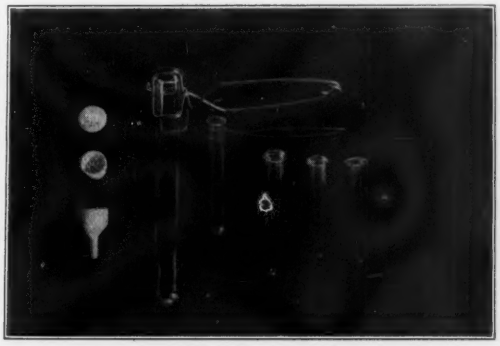


FIGURE 5.—MICRO CRUCIBLE AND COVER; MICRO FUNNEL (NOT NECESSARY); 15-CM. TEST-TUBE FOR SIZE COMPARISON; 3-ML. TEST-TUBE AND HOLDER USED IN THIS COURSE; 3-ML., 2-ML., AND 1-ML. CENTRIFUGE TUBES

The tests given for zinc were evidently not satisfactory and should be improved, or better ones substituted.

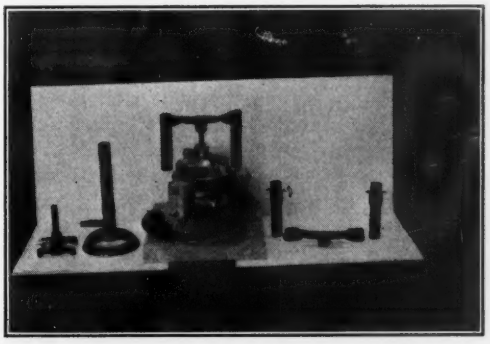
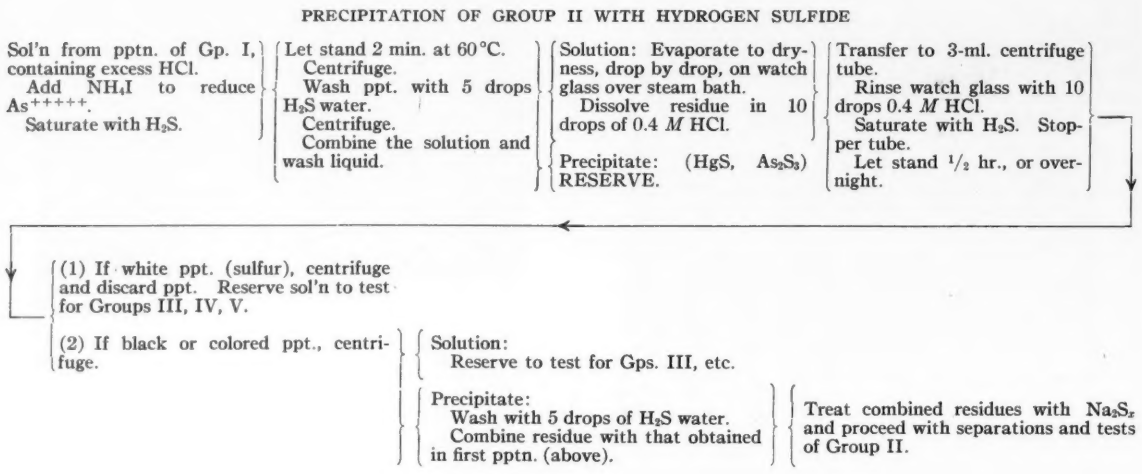


FIGURE 6.—ELECTRIC MICRO CENTRIFUGE, SHOWING ASSEMBLY OF CROSS-ARM AND TUBES. ALSO MICRO BURNER AND REGULAR BURNER TO SHOW RELATIVE SIZES

Zn proved to be the most elusive cation in the whole system of analysis.

In the case of cobalt, the percentage of incorrect results was due not to failures to detect the ion, but to the

fact that positive tests were often apparently obtained with the *alpha*-nitroso-*beta*-naphthol reagent when no Co was present. Several ions, namely cupric, ferric, silver, stannous, and bismuth, may precipitate with this reagent. Also, the reagent itself may precipitate upon dilution with water. In the latter part of the course, the results of the Co tests were much better.


PRECIPITATION OF GROUP II WITH HYDROGEN SULFIDE
Sol'n from pptn. of Gp. I, containing excess HCl.
Add NH_4I to reduce As^{+++++}.
Saturate with H_2S.
Let stand 2 min. at 60°C.
Centrifuge.
Wash ppt. with 5 drops H_2S water.
Centrifuge.
Combine the solution and wash liquid.
Solution: Evaporate to dryness, drop by drop, on watch glass over steam bath.
Dissolve residue in 10 drops of 0.4 M HCl.
Precipitate: (HgS, As_2S_3) RESERVE.
Transfer to 3-ml. centrifuge tube.
Rinse watch glass with 10 drops 0.4 M HCl.
Saturate with H_2S. Stopper tube.
Let stand 1/2 hr., or overnight.
(1) If white ppt. (sulfur), centrifuge and discard ppt. Reserve sol'n to test for Groups III, IV, V.
(2) If black or colored ppt., centrifuge.
Solution:
Reserve to test for Gps. III, etc.
Precipitate:
Wash with 5 drops of H_2S water.
Combine residue with that obtained in first pptn. (above).
Treat combined residues with Na_2S_x and proceed with separations and tests of Group II.

The difficulty with sodium ion was the usual one caused by its omnipresence in trace amounts in all of the solutions and chemical reagents. The ability to distinguish between traces of sodium impurities and actual presence of sodium ion in considerable amount was on litmus paper proved to be satisfactory, though not as sensitive as the Nessler reaction.

This was due, partly, to a more complete separation of Groups II and III by the improved method, and partly, no doubt, to the fact that the students had learned the necessity and value of thoroughly washing their precipitates when separations were made to insure removal of interfering ions.

Strontium was missed frequently when present, but was almost never reported present when absent. Probably the test for Sr is not sensitive enough for good results with small concentrations. A marked improvement in the Sr test, which is the precipitation of $SrSO_4$ with $(NH_4)_2SO_4$, was brought about after the students were directed to heat the solution to boiling and allow it to stand from five to ten minutes to aid in the precipitation of the $SrSO_4$. Although the textbook states that the tests for the alkaline earths, Ba, Sr, and Ca, are not as sensitive as most of the others, the results in the table indicate that the Ba ion, at least, was missed very infrequently.

The results on the mercuric ion were poor in the early analyses, but became quite satisfactory as the students gained experience.

In Group V, the NH_4, Na, and K ions all gave some trouble. In the case of the NH_4 ion, the trouble seemed to be due principally to the use of the very sensitive Nessler's reagent test. It was found that NH_4 ion could be detected in the distilled water stored in the laboratory, and was due to contamination by ammonia and ammonium salts present in the air. The common test for ammonium ion in which the solution is warmed with NaOH and the vapors tested by odor or by effect learned only by experience. The zinc uranyl acetate test and the flame test for sodium were used, and were fairly satisfactory when properly performed.

Failure to completely volatilize the ammonium salts before testing for potassium accounts for most of the trouble with this ion. The flame test for potassium was used with satisfactory results. The flame was viewed through a two-ounce flat medicine bottle filled with a saturated solution of chrome alum, which filtered out the flames of sodium and the alkaline earth metals and transmitted a red flash with potassium compounds. This procedure renders the test for potassium much more specific than the use of the cobalt glass filter recommended by the text.

Table 2 gives a summary of the results of analyses reported by five classes in macro qualitative analysis taught by the author, and of those reported by the class in semimicro analysis. It is seen that the averages are quite comparable. Actually, there appears to be a slight advantage in favor of the semimicro course.

TABLE 2
RESULTS OF CATION ANALYSES, MACRO AND SEMIMICRO

	Macroanalysis	*Semimicro Analysis*
Total number of tests made for all cations	3708	1193
Total number reported correctly	3111	1003
Percentage reported correctly	83.8	84.1

No attempt has been made to present a critical analysis of results of the anion tests. There is unquestionably much room for improvement here, both in the macro and in the semimicro courses. In place of the

present more or less random method of testing, a systematic scheme of separation should be worked out for the anions, as it has been for the cations. There is little doubt that the semimicro technic is just as applicable in anion as in cation analysis, but it has not as yet reached the same state of development.

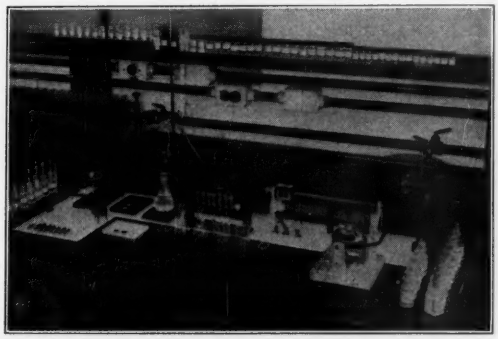


FIGURE 7.—COMPLETE EQUIPMENT FOR ONE STUDENT, SHOWING INDIVIDUAL REAGENTS

Figure 7 shows the complete assembly of equipment used by one student in the semimicro qualitative analysis course. With the exception of the centrifuge and a few bottles of stock test solutions, the apparatus shown is individual equipment, and is not shared by several students.

In conclusion, it has been found that the course in semimicro qualitative analysis is very satisfactory for the teaching of chemical principles and reactions. In addition, it is interesting and stimulating both to instructors and to students. The rapid growth and widespread interest in the use of this technic indicates its growing popularity, and, while there is still much to be done to perfect the presentation of the course and determine just what tests are most suitable for student use, this study is being carried on by a number of workers in the field.

It is hoped that the suggestions offered in this paper may prove of use to those who contemplate the adoption of the semimicro method of qualitative analysis instruction, and the author invites inquiry or suggestions from other teachers interested in this subject.

METHODS *for the* GRAPHICAL REPRESENTATION *of* QUATERNARY SYSTEMS INVOLVING RECIPROCAL SALT PAIRS, MAKING POSSIBLE *the* EXTRAPOLATION *of* TIE-LINES*

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INTRODUCTION

WHEREAS the usual methods of plotting quaternary systems of the ordinary type, namely those composed of water and three salts with a common ion, or of four oxides such as the systems occurring in glass and other complex silicates, make possible the direct application of Schreinemakers' method of residues[1] for the extrapolation of tie-lines and indirect determination of solid phases, the corresponding operation in quaternary systems involving reciprocal salt pairs is more difficult and necessitates certain special methods of plotting. The application of the wet residue method to the simpler type of quaternary systems was first explained by Schreinemakers himself;[2] simplification[3] and broader generalizations[4] have since been made by others. Morey[5] has pointed out that by the

* Presented before the Division of Physical and Inorganic Chemistry at the ninety-fourth meeting of the A. C. S., Rochester, New York, September 10, 1937.

[1] SCHREINEMAKERS, *Z. phys. Chem.*, **11**, 81 (1893).

[2] SCHREINEMAKERS, *ibid.*, **59**, 641 (1907).

[3] BELL, *J. Phys. Chem.*, **11**, 394 (1907).

[4] IGELSRUD AND THOMPSON, *J. Am. Chem. Soc.*, **58**, 2003 (1936).

[5] MOREY, *J. Phys. Chem.*, **34**, 1745 (1930).

use of determinants the method is directly extensible analytically to systems of still higher order, while recently F. Perel'man[6] has described a graphical application of the method to systems of any order.

For quaternary systems involving reciprocal salt pairs, however, the methods universally described in phase-rule texts for their graphical representation do not allow the determination of the composition of solid phases by the extrapolation of tie-lines. These methods are those of Löwenherz[7] and of Jänecke.[8] In that of Löwenherz, the units plotted are equivalents, or equivalent gram-molecules, of salts per fixed amount (1000 moles, usually) of water; in that of Jänecke, the units are moles of water per fixed amount (100 equivalents) of total salt. In either case the resulting solid isothermal figure has no definite dimensions, but extends to infinity; extrapolation is therefore impossible. The principle of extrapolation, which is merely the application, algebraic or graphical, of the method of residues of Schreinemakers, requires a finite, limited solid figure in which every point represents a fixed total amount of material or a fixed total number of units plotted. Schreinemakers[9] himself supplied a method for such an isothermal representation, which is adequate and at least as elegant as the method of Löwenherz both in solid representation and in projection. The method, nevertheless, seems hardly to have been used except by Schreinemakers himself, and is not noticed at all in the available texts. As a result the indirect determination of solid phases in this type of quaternary system has remained obscure, and has even brought about "original" attempts to solve the problem. Igelsrud and Thompson,[4] in illustrating a general analytical application of the Schreinemakers wet residue method to the ordinary type of quaternary system (water and three salts with a common ion), make the statement that the same method could be applied directly to systems containing metathetical components. This, however, is true only if certain methods of plotting are used, and the extrapolation is impossible, either algebraically or graphically, if the two exclusively described methods of representation are used, namely those of Löwenherz and of Jänecke.

The present writers, likewise in ignorance of Schreinemakers' own complete method, evolved, in connection with certain experimental work on reciprocal quaternary systems carried out in this laboratory,[10] a method for the representation of such systems which does make possible this necessary extrapolation for the indirect determination of solid phases. It is the purpose of this paper then to describe briefly this suggested method, and also to bring to the attention of workers in this field the still better and too neglected method described by Schreinemakers himself.

[6] PEREL'MAN, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. Chem.*, **1936**, 379; *Chem. Abstr.*, **31**, 3368 (1937).
[7] LÖWENHERZ, *Z. physik. Chem.*, **13**, 459 (1894).
[8] JÄNECKE, *Z. anorg. Chem.*, **51**, 133 (1906).
[9] SCHREINEMAKERS, *Z. physik. Chem.*, **69**, 557 (1909).
[10] HILL AND LOUCKS, *J. Am. Chem. Soc.*, **59**, 2094 (1937).

SCHREINEMAKERS' DIAGRAM

The diagram described by Schreinemakers for this purpose[9] is a symmetrical pyramid, with the altitude, or water axis, equal to half the base diagonal. Any point in or on the pyramid represents a total of 100 equivalents of the four components; the units plotted are then mole percentages (in which equivalent gram-moles are used) measured off, for water, along the vertical axis, and for the four salts, along the diagonals of the base, each corner of the base representing a pure salt. The figure is finite, regular, and unequivocal. Making use of the analysis of the saturated solution and that of the wet residue, Schreinemakers points out that the solid phases can be determined by graphical extrapolation on the projection of the tie-lines on two planes, the base and one of the diagonal vertical planes of the pyramid.

THE NEW DIAGRAM

The method of representation employed by the writers is similar to that just described, in that the four salts are plotted, likewise in equivalents, along two axes intersecting at right angles, and fixing the plane of the base of the solid figure; the water component is then plotted similarly along a vertical axis rising from the intersection of the two horizontal axes. The difference is that each point in this solid figure is made to represent 100 grams of total mixture, instead of 100 equivalents. This feature leads to certain differences in the two methods and perhaps, in some situations, to certain minor advantages, to be pointed out later.

Since any point in or on the isothermal figure is to represent a total of 100 grams of the four components, the length of each of the five axes, radiating from the origin (one for water, one for each of the four salts), will be fixed by the number of equivalents of each substance in 100 grams of the pure substance. The result, of course, is an irregular tetragon for the base, and an irregular pyramid for the solid isotherm. It is to be noted, however, that the only requirements for the extrapolation of tie-lines (and therefore for the possibility of the indirect calculation of solid phases) are (1) a finite figure for the isotherm, and (2) a definite, singular meaning for any given point in the figure. Symmetry is not required; the figure may be irregular. It must simply be three-dimensional, have finite limits, and have a single value for any point. In addition, the reciprocal nature of the salt pairs imposes the limitation that the units must be equivalents in order to meet the condition that the sum of the positive ions must equal the sum of the negative ions.

In Figure 1, showing the base of the isothermal figure, the points *A*, *B*, *C*, and *D* represent, respectively, 100 grams of the pure salts AN, BN, BM, and AM; they are then the corners of the base of the pyramid. The length of the vertical axis (or the altitude of the pyramid), raised perpendicularly to this base at the intersection O, is also limited, fixed by the number of equiva-

lents of water in 100 grams of water. The result therefore is an irregular pyramid for the complete isotherm.

Assigning the five substances to the axes as follows, A on $-x$, C on $+x$, B on $+y$, D on $-y$, and water on z, then in plotting a point P on this base, containing a equivalents of A, b of B, and c of C (and no water), per 100 g., the coördinates are $x = c - a$, and $y = b$. This, of course, is the same principle used both in the Löwenherz projection and in Schreinemakers' method. In general, for a mixture containing w equivalents of water, a of A, b of B, and c of C, the coördinates in the

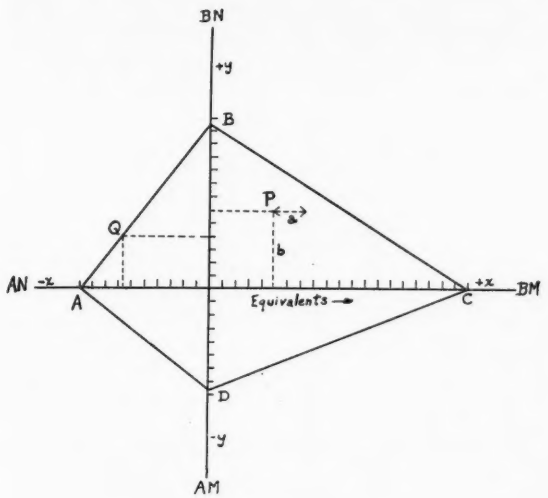


FIGURE 1

solid figure will be $x = c - a$, $y = b$, $z = w$. In practice the plotting of experimental data is actually simpler. Since the equivalents of water are not interchangeable (reciprocal) with those of any salt, the vertical water axis can be subdivided directly in terms of weight per cent. of water, the total length then simply representing 100 g. of water; 100 − wt. % of water then gives the number of grams of total salts present at the given level of the figure.

The elements of the solid figure may be interpreted as follows:

1. Points, or corners: the apex represents pure water; the corners of the base, the four pure salts.

2. The edges represent the eight binary systems of the complete quaternary system: four mixtures of two salts with a common ion, and four mixtures of water and each of the four salts. It can be shown that the weight ratio of the two components of these binary mixtures is represented directly by the relative position of the point on an edge. Thus for point Q in Figure 1, g. A/g. $B = QB/AQ$; or % $A = QB/AB$ and % $B = AQ/AB$.

3. The faces of the figure represent the five ternary systems of the complete quaternary system. The base is the ternary system consisting of the reciprocal salt pair itself; any point on the base represents 100 g. of such a mixture. To calculate the composition of a point P (coördinates x, y) on the base (see Figure 1), we note first of all that P may be calculated in terms of

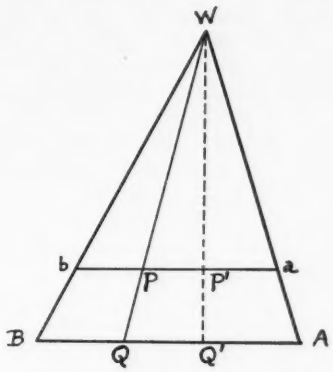


FIGURE 2

either B, C, and D or A, B, and C. In terms of A, B, and C, the calculation of the composition is made from the following set of equations:

y = equivalents of $B = b$ g./equivalent weight of B, or b/B
x = (equivalents of C) − (equivalents of A), $= c/C - a/A$
$a + b + c = 100$

The composition of points in other sections of the base, or on the axes or origin, can be similarly calculated.

The four side faces of the pyramid represent the four ternary systems of water and two salts with a common ion. These are all irregular, acute-angled triangles; but although irregular they have definite geometrical and mathematical properties, permitting the interpretation of these faces directly in terms of weight rather than equivalents. Thus for the point P in Figure 2, the composition in weight percentage is as follows:

$$\% H_2O = Q'P'/Q'W = QP/QW$$
$$\% A + \% B = 100 - \% H_2O$$
$$\% A/\% B = QB/QA = bP/aP$$

4. Finally, to obtain the composition of any point (x, y, z) in the interior of the solid pyramid, the equivalents of the salts (choosing one of the two sets of three salts available for any given point) per 100 g. can be calculated as shown above for points on the base of the figure, except that the total weight is no longer 100 but 100 − g. H_2O (calculated from or read from the coördinate z, depending on the units used for the z axis).

EXTRAPOLATION OF THE TIE-LINES IN THE SOLID ISOTHERMAL FIGURE

Such a diagram makes possible the direct application of Schreinemakers' method of residues for the extrapolation of tie-lines and determination of solid phases.

The extrapolation can first of all be made algebraically; by means of the usual analytical equations of straight lines in three-dimensional rectangular coördinates (with the composition variables represented as follows: x for C, $-x$ for A, y for B, $-y$ for D, and z for H_2O), the intersection of a tie-line with any given plane whose equation is known (such as the base, or a given level of the figure, etc.), can be determined by methods explained by Morey[5] and by Igelsrud and Thompson.[4]

Graphically, the extrapolation is found to be easier and more direct through the extrapolation of tie-lines projected on two intersecting planes of the figure. Whereas Schreinemakers[9] suggested the use of the base and one diagonal vertical plane for the graphical extrapolation, it has been found more convenient to make use of the two intersecting vertical diagonal planes alone, or the x-z and the y-z planes. The results thus obtained are very easy to interpret.

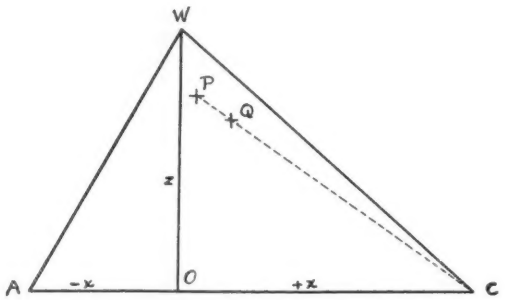


FIGURE 3.—THE x-z PLANE, $AWCO$

For example: a tie-line, fixed by two points P and Q (saturated solution and wet residue or original complex) may be projected on the two planes $AWCO$ (x-z) and $DWBO$ (y-z) as shown in Figures 3 and 4. In this case the extrapolation shows the tie-lines to intersect the base at the corner C; or the coördinates of the intersection with the base are $x = C$, for C, and $y = O$, for B and D. Therefore the phase, if anhydrous, is pure C.

The use of two intersecting diagonal planes in this manner actually makes extrapolation in reciprocal quaternary systems simpler, graphically, than in systems of water and three salts with a common ion, where the method described by Igelsrud and Thompson[4] appears to be much more complicated and cumbersome than this; in the latter systems Bell's method[3] will be found very useful.

To summarize some of the possibilities in the extrapolation:

If the phase is a pure anhydrous salt, the tie-lines intersect at one corner in the first plane and at the origin in the second.

For a compound of B and C, the tie-lines intersect at a definite point on OB in the first plane, and a definite point on OC in the second; and the total weight of B and C calculated from the equivalents of each at the intersections equals 100 g.; the phase therefore contains no A or D.

For a ternary or tetragene compound, the result of the extrapolation is similar to the foregoing except that the total weight of B and C will be less than 100 g.; the point will therefore lie inside the base, and its composition can easily be calculated.

For a solid solution of B and C, the tie-lines end on the line BC (in the solid figure); they start at B in the first plane and at O in the second, and go continuously to O in the first and to C in the second plane, always adding up to 100 g.

For a hydrate of B, the tie-lines in the first plane all intersect WB at a fixed point corresponding to the composition of the hydrate; in the second plane, the lines intersect WO at a point with the same value of z as in the first plane.

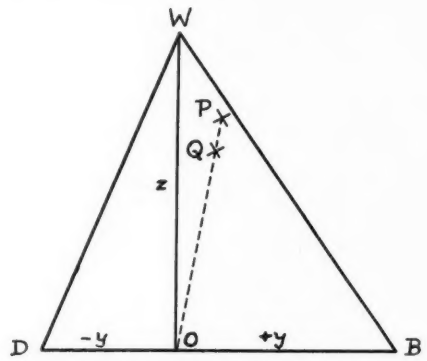


FIGURE 4.—THE y-z PLANE, $DWBO$

For a hydrated double salt of B and C, the tie-lines intersect, in the first plane, at a point inside the triangle WOB, and in the second plane, inside the triangle WOC: but the value of z will be the same in both planes.

ORTHOGONAL PROJECTION ON THE BASE

The three-dimensional quaternary isotherm obtained in either of these two methods of representation (that of Schreinemakers or that here suggested), may be projected, orthogonally, on the base of the pyramid, with a result similar to the familiar Löwenherz diagram. This being a projection of curved lines and surfaces, the crystallization paths appearing on the plane figure will likewise be curved, and similar to those in the Löwenherz projection. Finally, just as the latter diagram can be expanded into a Jänecke diagram, in which the salts (omitting water) are plotted on the basis of equivalents per 100 equivalents of total salts, the present projection can similarly be expanded to a Jänecke type of diagram, which however will be not a square, but an irregular tetragon of the same shape as the irregular base employed in the method. The crystallization paths, how-

ever, will now be straight lines, as they are in the Jänecke diagram, thus permitting the graphical determination of congruent points. The procedure for the geometrical expansion of the original projection into the Jänecke type of figure is described in Blasdale.[11] A true, square Jänecke diagram, on the other hand, will be obtained by the corresponding expansion of the projection of the quaternary isotherm plotted according to Schreinemakers' original suggestion, namely, on the basis of equivalent percentages.

REMARKS

While this older but unused method of Schreinemakers is adequate theoretically, for all purposes of representation and extrapolation, and obviously possesses the distinct advantage of symmetry over the new method suggested, there are nevertheless a few minor advantages in the use of the 100 gram figure which may be of some significance for certain special purposes. (1) The data can be plotted directly in terms of weight per cent. divided by the respective equivalent weights for the four salts, and simply weight per cent. for water, without having to calculate everything in terms of equivalent-mole fractions. This is of some advantage, as we have found, especially in extrapolating through the composition of prepared total complexes. (2) The edges of this solid figure represent directly the weight relationships in the eight binary systems, even though the interior is plotted in units of equivalents; the single salt solubilities are thus represented directly in weight fractions on the four pyramidal edges. (3) The four side faces likewise represent the ternary systems in terms of weight relations directly, as stated above, instead of mole fractions. (4) For certain calculations of isothermal evaporation and crystallization, when it may be desirable to extrapolate to the level of a certain fixed weight percentage of water, this method has the distinct advantage that the plane corresponding to a fixed water content is horizontal, parallel to the base, so that it may be defined by a much simpler analytical equation than a corresponding plane in Schreinemakers' figure. In the latter method of representation a plane parallel to the base has the rather impractical significance of a certain number of equivalents of water to a fixed total number of equivalents of salts.

[11] BLASDALE, "Equilibria in saturated salt solutions," Chemical Catalog Co., New York City, **1927**, pp. 122–3 and 141–2.

SUMMARY

1. With the methods usually employed for the graphical representation of quaternary systems involving reciprocal salt pairs, namely the methods of Löwenherz and of Jänecke, the extrapolation of tie-lines (Schreinemakers' method of residues), necessary for the indirect determination of solid phases without analysis, is not possible.

2. The requirements of a figure adequate for such extrapolation are discussed.

3. Two suitable methods are described, one due to Schreinemakers himself, in which the system is plotted in a regular pyramid in equivalent-mole fractions, and one, here suggested, in which the system is plotted in an irregular pyramid, in terms of equivalents of the components per 100 grams of mixture.

4. The important geometrical and algebraic properties of this new figure are explained, and the two methods are briefly compared.

CORRESPONDENCE

PYRENE

Dr. Ross A. Baker has transmitted the following letter to us.

"While looking through my copies of the JOURNAL OF CHEMICAL EDUCATION, I came across your book review of Dr. Briscoe's new 'Introduction to College Chemistry.'* We appreciate greatly your efforts to correct the loose statement made by Dr. Briscoe concerning our product. However, there is one thing I would like to call to your attention in this connection. In your discussions you use the phrase 'the liquid known as pyrene.' We do not want to run the risk of losing the monopoly of the use of our trademark and would be grateful to you if you would kindly drop a note to Dr. Otto Reinmuth, Editor of the JOURNAL OF CHEMICAL EDUCATION, to the effect that there exists a great importance to us in the difference between 'the liquid known as pyrene' and, say, the liquid of the brand 'Pyrene.' A brief note published in the JOURNAL OF CHEMICAL EDUCATION covering this point would easily straighten out this matter.

* BRISCOE, H. T., "An introduction to college chemistry," Houghton Mifflin Company, New York City, **1937**. *Cf.* J. CHEM. EDUC., **14**, 399 (Aug., 1937) for Dr. Baker's review of the book.

"In this connection I would like to call your attention to the article 'Lost Monopolies of Names and Things,' published by Mr. E. W. Leavenworth, on pages 1006–8 in the September, 1937, issue of *Industrial and Engineering Chemistry*, which deals with such contingencies, and which you might want to read."

CHEMICAL EQUATIONS

To the Editor:

DEAR SIR:

I wish to submit the following criticism of the article "On the Writing of Chemical Equations" which appeared in the JOURNAL OF CHEMICAL EDUCATION, **15,** 75 (1938).

It is my opinion that Mr. Jacobs is correct in stating that beginning students find equations practically, or entirely, meaningless when written in the "old way." However, if one discusses atomic structure and ion formation before the use of formulas and equations are introduced, the various concepts have a very real meaning to them. I was greatly surprised to note the manner in which the author proposed to remedy the situation. To begin with, may I ask whether one will find many teachers writing the equation for a neutralization reaction, or others involving electrolytes, without the use of the ions which are involved? Too, if one should chose to use molecular formulas would it not be far wiser to use bold type for the portion of each substance which undergoes change?* Thus, to use the illustration of the reaction between sodium hydroxide and hydrochloric acid which the author cited, and if one feels he must use molecular formulas and is to employ the proposed scheme, I think it would be much better to indicate that the hydrogen atom and the hydroxide group react to form water, since this represents what does take place.

A minor point which has always nettled me, personally, is the use of equality signs in equation writing. This practice may cause a common misconception in the mind of the student and should be avoided.

Another surprise which was noted was the naming of 1, 2, 3-trichloropropane as glyceryl trichlorhydrin. The name is a misnomer, and while it may have been in good usage sometime ago, I have failed to find it mentioned as such in five current texts. The reference to the hydrolysis of the above compound being written by use of molecular formulas is beyond me. Where will one find a teacher of organic chemistry who does not use structural or semistructural formulas?

Assuring you that I think the editors of the JOURNAL OF CHEMICAL EDUCATION are doing an excellent piece of work and with the belief that the article in question was published with the idea of provoking criticisms, this letter is humbly submitted.

RALPH E. SILKER

NEBRASKA STATE TEACHERS COLLEGE
CHADRON, NEBRASKA

* *Editor's Note.*—It was not possible in all cases to reproduce exactly the type differentiations employed in Mr. Jacobs' original manuscript. In this instance conventional boldface type was used in place of a font not available to us.

"PREPARATION OF CONSTANT-BOILING HYDROBROMIC ACID"

To the Editor:

DEAR SIR:

I always like your editorials. The paper on HBr in the April, 1937, issue of "JCE," page 189, has aroused me to write you. My feelings are the same as urged me to write Dr. Gordon, for which see "JCE" May, 1930.

We all know that iodine and bromine are the raw beginnings of all their compounds. Why, therefore, Mr. Editor, give us a paper starting with expensive KBr, pure H_2SO_4 and also mentioning red phosphorus, and adding $SnCL_2$ to give a chlorine impurity?

And that $10.00 I offered Dr. Gordon has not even made a ripple of a query. Well, all the students of 1930, I hope, have jobs, and you write for a new crowd; perhaps a bright student in the sticks can still win it. What do you say?

Students seem in a vacuum, becoming aware only when they enter the outer world of pressure of costs. This paper on HBr is a case in point. "I&EC" quotes Br at 30¢, HBr 10% at 18¢. So 100% HBr on this basis is six times the HBr price or nine times the KBr at 31¢ and twelve or more the KBr price using H_2SO_4, etc., and, of course, the $KHSO_4$ would be wasted. (Laboratory prices much higher.)

In my paper which Dr. Gordon kindly published (*q.v.*) I gave the method used—simplicity itself—fully in a paper read before the British Pharmaceutical Conference at Dublin thirty-seven years ago, I think, since when the H_2S, SO_2 processes have been abandoned. I humbly ask you as an educational authority why my process has not just naturally seeped into the textbooks. Your authors, Heisig and Amdur, mention the literature, but what I should like to know and alter is, how their pure minds never once raised the question, "How does the manufacturer?" No, they mention red phosphorous (40¢, case lots), but omit the fumes.

The reagent firms are keen competitors, as your advertisements prove. They must make a profit. Their products are made with the cheapest raw materials, the least time, labor, and plant set-up, for the "best" product must be best from all points. But the chief point is the cost, setting the price.

Granted that laboratories buy many products obtained only by mass production, still, many inorganics used in first-year courses could be made by the advanced students to their very great advantage, in thought and training and at a saving in school money which is always below staff requirements.

At this length I have cooled off my feelings and it has just struck me that a small book giving the preparation of a couple of hundred or less chemicals, easily made in the ordinary laboratory, as pure and cheaper than the purchased article, would be worth while. My paper of May, 1930, gives the idea.

Also the recovery of wastes. For instance—a plant in California, 1917. Cobalt acetate, no supply from the East on THREE MONTHS OLD ORDER. Only one bottle left. Chemists worried. In the plant I heard it. Carried in a pot—"Cobalt wastes here." In two days there was all the salt they needed, and how they marveled. It was my turn to marvel that no one had thought it possible. Now, why did the chemists take it for granted that the stock shelves replenished themselves by magic. I ask you?

Is there such a book? Is it worth while? Would it do any good? Well, after this blow-off I will go to sleep for another seven years.

ERNEST M. MARSHALL

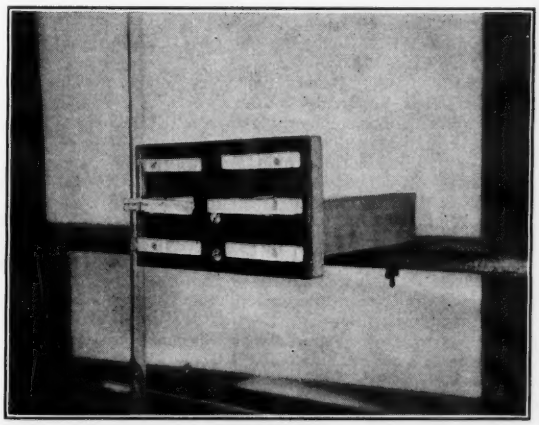
AN INEXPENSIVE BURET HOLDER

OLUS J. STEWART

University of Kentucky, Lexington, Kentucky

THE buret holder herein described evolved from an urgent need for a dozen holders to be produced in a short space of time at the lowest cost. The resulting product was so simple and satisfactory that it seemed desirable to bring the matter to the attention of others who might be interested. The photograph* shows the essential parts. A wooden arm, approximately 1″ × 2″ × 11″, bolted at one end to a shelf standing 16″ above the laboratory table, carries at its other end a block of wood, approximately 3.5″ × 6.5″ × 7/8″, to whose face is fastened by means of screws, four spring-type clothespins, two of which are disassembled. More specifically, with regard to the arrangement of clothespins, it may be said that each half of a disassembled pin, fastened with screws near the top and bottom of the front face of the block, serves respectively as the upper and lower support, while a whole clothespin, fastened mid-way between the aforementioned halves in such a way that the grooves of all parts are in a vertical line, completes the assemblage. A certain amount of rasping is required to provide clearance for burets of large diameter.

* The writer is indebted to Mr. Gino A. Ratti who prepared the photograph.



To operate the device one merely presses with the finger upon the lever of the central clothespin and simultaneously inserts or withdraws the buret. A buret may also be moved up, down, or even withdrawn from the holder for reading without depressing the lever. The serviceableness of the device cannot be gaged by its homely appearance and its cheapness. Although the cost of material for one holder is only a dime, many students prefer it to holders costing fifty times as much. The construction is rugged, a portable supporting stand is not required if a shelf is available, there is a notable absence of corrodible parts, and repairs may be effected easily with materials available everywhere at nominal cost.

ISOTOPES AND ANALYTICAL STANDARDS—A CORRECTION

As the result of an omission the value of hydrogen was incorrectly stated in this note [J. CHEM. EDUC., 15, 290 (1938)]. It should have been given as 1.0081.

CHANGING CONCEPTION *of* TEACHING HELPS *in* COLLEGE GENERAL CHEMISTRY TEXTBOOKS

RALPH E. DUNBAR

North Dakota Agricultural College, Fargo, North Dakota

EDUCATIONAL progress and improved methods of teaching should be reflected in the type and amount of teaching helps contained in representative general chemistry textbooks published over a period of several years. The present study was designed to ascertain what teaching helps show a noticeable variation as to occurrence; what teaching helps have remained constant as to occurrence; and what teaching helps have noticeably increased as to occurrence in recent years. Simmons[1] reports a similar investigation of sixteen general science textbooks published over a period of twenty-four years. For ease of interpretation, the twenty-four years covered in this previous analysis were divided into four equal periods. General science textbooks of four publishers were used for each period. A tabulation was made of sixteen distinct types of teaching helps revealing the different types of aids for each period, as well as indicating total frequency of occurrence for all periods.

In the present study a tabulation has been made of twenty-five college general chemistry textbooks, so selected that the copyright date for one year occurs only once during each of the past twenty-five years, 1912–1936 inclusive. An attempt has been made to select only books that are truly representative of the year in which each was copyrighted. By this procedure we have a representative sampling of college general chemistry textbooks for each of the past twenty-five years. Obviously, by such a plan it has been impossible to include many leading texts of these several years, since only one was selected for each year, and frequently several books were copyrighted during the same year. Likewise, later editions of many of these textbooks have since been published, but these older editions have been included as being representative of the several years involved. The following twenty-five textbooks designed for introductory work in college general chemistry have been included in this study.

NEWTH, G. S., "A text-book of inorganic chemistry," Longmans, Green and Co., New York City, **1912.**

BLAKE, J. C., "General chemistry, theoretical and applied," The Macmillan Co., New York City, **1913.**

OSTWALD, WILHELM AND ALEXANDER FINDLAY, "The principles of inorganic chemistry," Macmillan and Co., Limited, London, **1914.**

SMITH, ALEXANDER, "General chemistry for colleges," The Century Co., New York City, **1915.**

HOLLEMAN, A. F. AND HERMON CHARLES COOPER, "A text-book of inorganic chemistry," John Wiley & Sons, Inc., New York City, **1916.**

BYERS, HORACE G., "Inorganic chemistry," Charles Scribner's Sons, New York City, **1917.**

HILDEBRAND, JOEL H., "Principles of chemistry," The Macmillan Co., New York City, **1918.**

NOYES, WILLIAM A., "College textbook of chemistry," Henry Holt and Co., New York City, **1919.**

MCCOY, HERBERT M. AND ETHEL M. TERRY, "Introduction to general chemistry," McGraw-Hill Book Co., Inc., New York City, **1920.**

PARTINGTON, J. R., "A text-book of inorganic chemistry for university students," Macmillan and Co., Limited, London, **1921.**

LOWRY, T. MARTIN, "Inorganic chemistry," Macmillan and Co., Limited, London, **1922.**

DEMING, HORACE G., "General chemistry," John Wiley & Sons, Inc., New York City, **1923.**

GARARD, IRA D., "Applied chemistry," The Macmillan Co., New York City, **1924.**

NEWELL, LYMAN C., "College chemistry," D. C. Heath and Co., New York City, **1925.**

CADY, HAMILTON P., "General chemistry," McGraw-Hill Book Co., Inc., New York City, **1926.**

MCCUTCHEON, THOMAS P. AND HARRY SELTZ, "General chemistry," D. Van Nostrand Co., Inc., New York City, **1927.**

BLANCHARD, WILLIAM MARTIN, "An introduction to general chemistry," Doubleday, Doran & Co., Inc., Garden City, New York, **1928.**

FOSTER, WILLIAM, "Inorganic chemistry for colleges," D. Van Nostrand Co., Inc., New York City, **1929.**

SCHLESINGER, H. I., "General chemistry," Longmans, Green and Co., New York City, **1930.**

KENDALL, JAMES, "Smith's introductory college chemistry," The Appleton-Century Co., New York City, **1931.**

HOPKINS, B. SMITH, "Essentials of college chemistry," D. C. Heath and Co., New York City, **1932.**

NAYLOR, NELLIE M. AND AMY LE VESCONTE, "Introductory chemistry with household applications," The Appleton-Century Co., New York City, **1933.**

MCPHERSON, WILLIAM AND WILLIAM EDWARD HENDERSON, "An elementary study of chemistry," Ginn and Co., New York City, **1934.**

CARTLEDGE, G. H., "Introduction to inorganic chemistry," Ginn and Co., New York City, **1935.**

HOLMES, HARRY N., "General chemistry," The Macmillan Co., New York City, **1936.**

These twenty-five general chemistry textbooks are the product of thirteen separate publishers and are be-

[1] SIMMONS, MAITLAND P., "Changing conceptions of teaching helps in general science textbooks," *Science Educ.*, **20**, 211–4 (1936).

TABLE 1

TEACHING HELPS OCCURRING IN COLLEGE GENERAL CHEMISTRY TEXTBOOKS

Author of Textbook	*Newth*	*Blake*	*Ostwald*	*Smith*	*Holleman*	*Byers*	*Hildebrand*	*Noyes*	*McCoy-Terry*	*Partington*	*Lowry*	*Deming*	*Garard*	*Newell*	*Cady*	*McCutcheon*	*Blanchard*	*Foster*	*Schlesinger*	*Kendall*	*Hopkins*	*Naylor*	*McPherson*	*Carlledge*	*Holmes*	*Total Frequency*
Copyright Date	*1912*	*1913*	*1914*	*1915*	*1916*	*1917*	*1918*	*1919*	*1920*	*1921*	*1922*	*1923*	*1924*	*1925*	*1926*	*1927*	*1928*	*1929*	*1930*	*1931*	*1932*	*1933*	*1934*	*1935*	*1936*	
TEACHING HELPS																										
1. Pictures	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	25
2. Graphs	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	25
3. Tables	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	25
4. Topic Surveys	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	25
5. Key Words	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	25
6. Demonstrations	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	24
7. Key Statements	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	24
8. Footnotes	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X		X	X	23
9. Summaries			X	X	X	X	X	X	X	X	X	X		X	X		X	X	X		X		X	X	X	19
10. Exercises				X		X	X	X		X		X	X	X		X	X	X	X	X	X	X	X	X	X	18
11. Problems	X			X		X	X	X	X	X		X		X		X	X	X	X			X	X	X	X	18
12. Questions				X		X	X	X		X		X	X	X		X	X	X	X	X	X	X	X	X	X	18
13. Experiments	X	X	X	X				X		X		X	X	X			X	X	X	X	X	X	X		X	17
14. Atomic Weight Table in Cover				X	X	X		X	X			X	X	X	X			X	X	X	X	X	X	X	X	17
15. Large and Small Type in Text	X	X			X	X				X	X	X		X		X		X	X	X	X	X	X		X	16
16. Appendix	X					X						X		X				X	X	X	X	X	X	X	X	12
17. References	X	X								X			X					X	X		X		X		X	9
18. Periodic Table in Cover								X	X	X		X			X			X			X				X	8
19. Review Suggestions												X								X		X			X	4
20. Solubilities in Cover				X								X							X	X						4
21. Atomic Structure Table in Cover																									X	1
22. Electrochemical Series in Cover																					X	X				1
23. Spectra in Cover										X																1
24. Melting Points in Cover								X																		1

lieved to be a fair sampling of the average texts of the past twenty-five years. From a careful examination of the same, a tabulation has been made of twenty-four different types of teaching helps. These have been arranged in the order of frequency in Table 1.

A very common practice in the preparation of college general chemistry textbooks is the inclusion of valuable reference material, usually in tabulated form, in an appendix near the end of the book. In fact, the frequency and variation of this type of material in twelve of the twenty-five textbooks studied made it seem advisable to make a more detailed study of this type of material. In six more of the twenty-five textbooks such tabulated data was assembled on extra pages near the beginning or end of the book without being specifically designated as an "Appendix." Thus a total of eighteen out of the twenty-five texts contained valuable reference material for teacher and student use, assembled in a separate appendix or its equivalent, near the beginning or end of the book. This practice is surely to be commended, and the amount of such tabulated data has been very noticeably increased both as to frequency and amount in those textbooks of recent years, as an inspection of item sixteen in Tables 1 and 2 will reveal. A tabulation of this type of material is included in Table 2. This tabulation includes both that type of reference material listed under the title of "Appendix" and also similar material included in extra pages outside the main body of the text. The prevalence of atomic weight tables, periodic tables, and similar items included within the cover pages of the texts has been included under suitable headings in Table 1 only.

An examination of Table 1 indicates that pictures, graphs, tables, topic surveys and key words, each appearing twenty-five times, have been used rather consistently in college general chemistry textbooks over a period of the past twenty-five years. Suitable pictures offer an effective means of giving definite impressions and should be carefully selected and logically used. Line drawings of laboratory equipment and industrial photographs predominate. Statistical data, assembled in graphs and condensed tables, offer a convenient method of presenting items of related information. Topic surveys aid in correlating facts of importance, and their common and continued use indicates something of their value. Key words help principally in organizing the material presented or in emphasizing important terms or ideas.

Directions for demonstrations, either definitely outlined or sufficiently suggested for teacher's use, appear in twenty-four of the texts. Key statements, also appearing in twenty-four of the textbooks, are closely related to key words in frequency and use. Footnotes are used in twenty-three instances to elaborate or qualify statements appearing in the main body of the text. Summaries which should be a valuable aid to students in organizing the contents of the several chapters, and with a frequency of nineteen, appear rather consistently throughout the period of twenty-five years. However, a more detailed examination of the texts very definitely indicates a marked improvement in this respect in recent years, both as to quantity and quality of these summaries, if not in frequency of texts. Exercises, problems, and questions for student use are closely related. These occur somewhat more frequently in recent years and again there is also a noticeable improvement in the quantity and quality of these teaching helps in the textbooks of recent years. Total frequency for all is eighteen.

The frequency of experiments, namely seventeen, re-

mains relatively well distributed throughout the period of twenty-five years. However, the amount of student experiments in recent volumes has greatly decreased. There is a tendency in later years to place experimental work for student use in separate laboratory manuals rather than in the text itself. Recent volumes show a noticeable tendency to include atomic weight tables in the cover pages for ready reference use. The use of large and small type in the body of the text for purposes of emphasis has been a common practice for years, with some increase in frequency and amount in recent years. A very noticeable tendency of the past decade or so is to include a large amount of useful statistical information in tabulated form in a separate appendix at the end of the book. Twelve texts, eight of which were published during the past eight years, contain such sections. A more detailed account of these appendixes is given in Table 2. Other items in order are references, periodic tables in cover pages, review suggestions, solubilities in cover, with frequencies ranging from nine to four and with a decided tendency to predominate in recent years. Atomic structure tables, electrochemical series, spectra plates, and melting-point tables, each with a frequency of one, are variously scattered throughout the period covered in this study.

Table 2 is practically self-explanatory. The variety of material included in the several appendixes is extensive, as indicated. Six of the textbooks, designated by asterisks, do not include an appendix, designated specifically as such, but contain corresponding pages devoted to similar tabulated material. The type and amount of this material has noticeably increased in recent years. Vapor pressure tables heads the list in order of frequency, followed by metric and English units of weight and measure, physical constants of gases and elements. Other topics follow in decreasing order of frequency as tabulated until a list of some seventeen items occur, no one of which appears more than once in all of the textbooks studied.

TABLE 2

TEACHING HELPS OCCURRING IN APPENDIXES AND SIMILAR PAGES

Author of Textbook	Newth	Blake	Ostwald	Smith	Holleman*	Byers	Hildebrand	Noyes	McCoy-Terry	Partington	Lowry*	Deming	Garard*	Newell	Cady*	McCutcheon*	Blanchard*	Foster	Schlesinger	Kendall	Hopkins	Naylor	McPherson	Carlidge	Holmes	Total Frequency
Copyright Date	1912	1913	1914	1915	1916	1917	1918	1919	1920	1921	1922	1923	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	
1. Vapor Pressure—H_2O						X						X	X	X			X	X		X		X	X	X	X	11
2. Metric-Eng. Units						X								X				X		X	X	X	X		X	8
3. Phys. Const. Gases												X						X	X		X	X	X		X	7
4. Phys. Const. Elements						X												X	X		X		X		X	6
5. Temperature Scales						X						X						X		X	X					5
6. E.M.F. Series Metals																		X				X	X	X		4
7. Solubility-Solids																			X			X	X			3
8. Hydrogen Ion and pH													X									X			X	3
9. Logarithms														X				X						X		3
10. Atomic Weight Table											X					X										2
11. Periodic Table					X														X							2
12. Phys. Const. Comp.																		X	X							2
13. Solubility-Gases																			X				X			2
14. Scale of Hardness																		X		X						2
15. Spectra Plates					X										X											2
16. Energy, Power and Pressure Units						X						X														2
17. Heats of Combustion												X						X								2
18. Bibliography												X						X								2
19. Radium-Radioactivity	X																									1
20. Isotopes																							X			1
21. Mathematical Aids														X												1
22. Valence of Elements																				X						1
23. Solubility Products																									X	1
24. Crystallography																							X			1
25. Composition of Terrestrial Matter											X															1
26. Composition-Alloys						X																				1
27. Conductivity-Metals						X																				1
28. Sources of Chemicals																					X					1
29. Equilibrium Potentials												X														1
30. Other Names for Chemical Substances												X														1
31. Cost of Chemicals																									X	1
32. Composition and Fuel Value of Foods												X														1
33. Preparation of Colloidal Solutions												X														1
34. Noteworthy Events in History of Chemistry												X														1
35. Nobel Prize Winners																									X	1

* No "Appendix" designated specifically as such but the textbook contains corresponding pages devoted to similar tabulated material.

CONCLUSIONS

In addition to the facts immediately obvious from a study of Tables 1 and 2, the following conclusions seem to be justified.

1. Supplementary teaching helps, as tabulated in Table 1, have consistently increased in quality and quantity in college general chemistry textbooks during the past twenty-five years.

2. The items of summaries, exercises, problems, questions, and review suggestions, designed especially for student study and use, have increased noticeably during recent years in these representative textbooks.

3. Numerous other teaching helps, particularly those heading the list in Table 1, run surprisingly uniform in these textbooks, published over a period of twenty-five years.

4. Recent texts show a marked tendency to utilize the four pages within the covers for supplementary tables and reference material.

5. Large amounts of statistical data are assembled in separate appendixes in recent volumes.

6. The wide variation and lack of uniformity in the material in these appendixes are particularly noticeable.

A STATISTICAL EVALUATION *of* STUDENT GRADES *in* QUANTITATIVE ANALYSIS*

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ONE of the problems which, I suppose, nearly always puzzles the professor of quantitative analysis is that of assigning a suitable grade to his students for their laboratory work. John Doe is given a sample of iron ore for analysis; after applying himself to this baffling problem for a week or so John tells the professor that he is willing to stake his reputation as a chemist (such as it is) that the sample contains 59.75 per cent. of iron. The professor is reasonably certain that it should analyze 59.16 per cent. What grade (on the basis of 100) shall he write down for John's analysis, which differs from "the theory" by 10 parts per 1000 of iron? I propose in this article a solution of this problem which I have found very useful. The general method used may be employed by anyone confronted with a similar problem; the actual figures themselves will be more or less exactly applicable according to the degree of correspondence between any given set of conditions and those under which these figures have been derived.

I make the fundamental assumption that the student should be "tried by a jury of his peers." That is to say, I judge the performance of my present students not by comparison with that of the Bureau of Standards nor with that of any veteran analyst, but by comparison with the results which have been obtained by former students working under the same conditions. The apparatus and methods used and the supervision over the students are all about the same as is usually considered standard practice in a beginning class in quantitative analysis. If John Doe's error of 10 parts per 1000 represents the same discrepancy as was reported by some dozens of his predecessors, John has done an average job and should get an average mark, which I take to be 75 per cent.; if his error is smaller or larger than the average error of his predecessors he should get a correspondingly higher or lower mark, respectively. The actual evaluation of these marks is based on a statistical study which will be described presently.

First, however, it will be necessary to set forth briefly the conditions under which the actual figures were obtained. The class performs the following volumetric analyses:

TABLE 1

Sample to be analyzed	*Constituent reported*	*Standardising agent*	*Method*
Soda ash	Na_2CO_3	Na_2CO_3	Methyl orange indicator
Acid (solid or liquid)	Acidity	Standard acid	Phenolphthalein indicator
Iron ore	Fe	$Na_2C_2O_4$	Zimmerman-Reinhardt
Pyrolusite	MnO_2	Same	Decompose with excess $Na_2C_2O_4$ + H_2SO_4
Crude copper oxide (or a copper salt)	Cu	KIO_3	Iodimetric
Crude arsenic oxide	As_2O_3	As_2O_3	Same
Soluble chloride	Cl	KCl	Volhard

Those who continue quantitative analysis in the second term perform a gravimetric determination of sulfur and the complete analysis of a limestone and a brass; but I shall confine myself in this present article to the volumetric procedures, the statistical data for

* Presented before the Division of Chemical Education at the ninety-third meeting of the A. C. S., Chapel Hill, North Carolina, April 13, 1937.

which are more securely established. The students use the regular standard laboratory apparatus, but are not required to calibrate their weights or their burets, and this for two reasons. First, it is, in my experience at least, useless; with all due respect to the capabilities of our young men, I fear that the "corrections" which they would thus introduce would in most cases put them farther off the track than would the actual calibration errors of the manufacturer, which are usually of the order of 1 or 2 parts per 1000 at the most. Secondly, it is bad pedagogy; to my way of thinking there is no surer way to disgust beginning students with analytical chemistry than to require them to perform a tedious uninteresting task which turns out to be of little or no practical value to them in their laboratory work. It seems to me that the time thus consumed could be more profitably spent in becoming acquainted with a few more chemical procedures which they will certainly have to make use of later in medical school or in more advanced courses in chemistry. Another and very practical objection is that if the calibration is to mean anything the professor should be able to check the student's result against that obtained by an experienced person, just as is the case with the "unknowns" themselves. Once one of these has been analyzed by one of the staff the result holds good until the sample has been used up; but my assistant and I have too much to do to run "analyses" on about one thousand seven hundred individual weights, not to mention about two hundred fifty glass "unknowns" which are never used up but which more or less quickly meet a violent end on the laboratory floor. In short, I believe that calibration of weights and glassware, what with the present high standards of the apparatus manufacturers, should be left to the courses in physical chemistry or advanced analytical chemistry. That this practice is justified in the long run is shown in the next paragraph.

In order to estimate student performance in quantitative analysis by a statistical method it is, of course, necessary to establish that their errors are not constant, but rather that these are random, accidental, non-controllable errors, such as are amenable to a statistical treatment using the normal curve of probability. This test may be applied by comparing the means of many student analyses on given samples with the values established for these samples by one or more experienced analysts. The "unknowns" for the students' analyses were purchased from several different laboratories specializing in this sort of work, and many of them (in some case all of a given series) were analyzed by myself or others of our staff to see what certainty could be ascribed to the analyses given on the manufacturer's certificate. The mean values obtained by the students on these samples were then computed. One would expect to find good agreement between two competent analysts on a simple determination, but the striking fact that came out of these comparative results was that the students in the long run and despite the scatter in their individual results obtained mean values in very close agreement with those of more experienced chemists. Some of these comparisons are given in the following table.

TABLE 2

COMPARATIVE ANALYSES ON STUDENT "UNKNOWNS" FOR ELEMENTARY QUANTITATIVE ANALYSIS

Sample	*Manufacturer's analysis*	*Professor's analysis*	*Students' analysis*	*Number of student results averaged*
Soda Ash No. 1	98.71	98.70	98.83	17
Soda Ash No. 2	34.28	34.25	34.32	26
Soda Ash No. 3	26.57	26.54	26.56	18
Iron Ore No. 1	21.63	not run	21.68	20
Iron Ore No. 2	28.33	not run	28.29	20
Iron Ore No. 3	42.80	42.73	42.88	8
Pyrolusite No. 1	75.74	75.51	75.64	19
Pyrolusite No. 2	66.88	not run	66.84	25
Copper Salt No. 1	55.02	55.06	55.06	18
Copper Salt No. 2	53.76	53.63	53.75	11
Arsenious Acid No. 1	19.87	19.98	19.96	24
Arsenious Acid No. 2	35.73	35.72	35.69	22
Soluble Chloride No. 1	27.98	27.77	27.74	5

This reasonably close correspondence between the results obtained by experienced chemists working with calibrated apparatus and those obtained by beginning students using no calibration corrections is probably about as good as one would expect, and clearly shows the absence of any serious constant error that would preclude a statistical treatment.

In order to get a fair estimate of the actual dispersion of the results of individual students for any given determination it is necessary to work up all the individual reports made on at least one or two samples of the determination in question over a period of several years. For each series of individual reports the mean and the deviation of each individual result from this mean is then calculated, from which one obtains the standard deviation of the series by the expression

$$S = \sqrt{\frac{\Sigma d^2}{N-1}}$$

Where S is the standard deviation of the individual results, Σd^2 the sum of the square of the individual deviations from the mean of the series, and N the number of individual reports in the series. By performing these operations on at least two, and in some cases four, series of individual student reports on all the volumetric determinations previously listed I have calculated the standard deviations for each one. These are set forth in the following table, which gives the arithmetic mean of two or more values for the standard deviation for each

TABLE 3

STANDARD DEVIATIONS (IN PARTS PER 1000) OF STUDENT RESULTS ON QUANTITATIVE UNKNOWNS

Determination	*S (p. p. 1000)*
Acid; Cu salt Pyrolusite; Arsenic	6
Soda ash; sol. chloride	7
Iron ore	8

determination, expressed in parts per 1000 of the constituent being determined, and rounded off to the nearest unit of S.

According to the grading system which I am here describing, a student whose report differs from "theoretical" by an amount equal to the standard deviation for that particular determination will be given the grade of 75; he has done an average job, no better and no worse than that done by his predecessors. Between 75 and 100 per cent. there are five intervals of five points each, the whole interval of 25 units of grade corresponding to the standard deviation. Hence we may assign each five-point interval the corresponding value $^5/_{25} = 0.2S$; this makes the lowest acceptable mark (60 per cent.) come out to $\frac{100-60}{5} \times 0.2 = 1.6S$. That is to say, there are 8 intervals, each lowering the grade by five points, between 60 and 100 per cent., each interval corresponding to $0.2S$. The fundamental table of grades as a function of S thus comes out to be:

TABLE 4

Grade	*Discrepancy between student's report and the "theoretical" result as a function of S, in parts per 1000*
100	0.0
95	0.2 S
90	.4 S
85	.6 S
80	.8 S
75	1.0 S
70	1.2 S
65	1.4 S
60	1.6 S

It is generally stated that if an individual measurement differs from the mean of the series by approximately twice the standard deviation (or what is practically the same thing, by three times the probable error) of the individual measurements, that particular measurement should be rejected, since there are only 46 chances in 1000 that it belongs to the series; the statistical odds corresponding to a discrepancy of $2S$ are 21 to 1 against such a measurement being a valid member of the series. In the above scheme of grading, the criterion of rejection is set at 1.6 times the standard deviation, corresponding to 110 chances in 1000 in its favor, or 8 to 1 against it; however, I do not think that this is excessively rigid.

Once the dispersion of the students' results on a given determination has been calculated (*i. e.*, the standard deviation expressed in parts per 1000) Table 3 and Table 4 may be combined to give the actual table which I use to grade the students on their volumetric determinations.

The original reports of individual students upon which these figures are based are not the results of isolated single analyses; all are averages of two or more individual determinations, which in turn are based on two or more standardizations of the solution being used. Naturally, I will not accept a reported result which is an average of two or more highly discrepant analyses; the duplicate determinations should agree reasonably well, but how close this agreement should be is not easy to decide on a statistical basis. If the average of the two or more determinations reported

TABLE 5

Grade	*Discrepancies of Students' Reports, in p. p. 1000*		
	on acid, MnO_2, Cu, As (S = 6 p. p. 1000)	*on Na_2CO_3, Cl* (S = 7 p. p. 1000)	*on Fe* (S = 8 p. p. 1000)
95	1.2	1.4	1.6
90	2.4	2.8	3.2
85	3.6	4.2	4.8
80	4.8	5.6	6.4
75	6.0	7.0	8.0
70	7.2	8.4	9.6
65	8.4	9.8	11.2
60	9.6	11.2	12.8

by the student agrees with the accepted value for the unknown within $1.6S$, but his determinations show a difference of let us say $2.5S$ between the maximum and minimum, he is told to go over the process again, checking first the arithmetic and next the chemistry, since his agreement with the true value is only fortuitous. Ordinary experience is as good a guide as anything in this matter of the agreement of duplicates. What is ultimately desired is a close agreement between the analysis and the true composition of the material being analyzed; ordinarily, the close agreement of individual determinations run according to a standard acceptable method is one's only assurance that such objective conformity of analysis to composition has been attained. This relation of accuracy to precision—of the objective to the subjective aspect—should be explained to the students so they will understand why highly discrepant analytical results are not acceptable, even though their mean value may be acceptable. I usually tell them that as analysts just beginning they can ultimately depend upon me to tell them whether or not they are right; but if they do analytical work later, on commercial products or on research substances, the case is just reversed—someone else will be asking them.

In conclusion I wish to acknowledge my indebtedness to Dr. Jack W. Dunlap, Associate Professor of Education in the Fordham Graduate School, who has been most generous of his time and effort in helping me acquire some knowledge of statistical theory, of which this present article is of course a very minor, but, I trust, useful application.

. . . . . The character of the true philosopher is to hope all things not impossible, and to believe all things not unreasonable. He who has seen obscurities which appeared impenetrable in physical and mathematical science suddenly dispelled, and the most barren and unpromising fields of inquiry converted, as if by inspiration, into rich and inexhaustible springs of knowledge and power on a simple change of our point of view, or by merely bringing to bear on them some principle which it never occurred before to try, will surely be the very last to acquiesce in any dispiriting prospects of either the present or future destinies of mankind . . . . . —SIR JOHN HERSCHEL

WHY SOLVE *for* X?*

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THE average student in college freshman chemistry courses is arithmetically infantile. The so-called "mathematical difficulties" in such courses are almost entirely matters of seventh- and eighth-grade arithmetic. College freshmen can do problems of this grade by an automatic process if the labels on the quantities are those of everyday life, but fail completely if they are unfamiliar. With many students, it is not necessary to go as high as the seventh grade to find this state of affairs. Say, "There are 12 eggs in a dozen, how many dozen in 42 eggs?" The student answers, "Three and a half." But say, "There are 12 g. of carbon in a gram atom of it, how many gram atoms of carbon in 42 grams?" and you find that the student doesn't know whether to divide 12 by 42 or to multiply. I have even said to a student, "If one mole is two equivalents, how many moles is one equivalent?" and more than once been answered, "Two."

For the benefit of a dean who seemed to be taking freshman complaints of mathematical difficulties in Chemistry 1 at their face value, I once devoted the opening session of the course to a little examination in grade school arithmetic. The hardest problem ran, "If a car can go 80 miles on a dollar's worth of 18¢ gasoline, how far could it go on a dollar's worth of 16¢ gasoline?" Sixty per cent. of the class got below sixty per cent. of the quizz. It is true that this was in a college for women, but I have been assured by a well-known professor at Yale that the situation is no different there.

The one process involving arithmetical reasoning which any considerable number of students can employ in solving problems is what our fathers called, "the rule of three," ratio and proportion. There seems something particularly appealing in the orderly design of dots. On the other hand an even larger number than use the dots, use the equivalent form in which the ratios are expressed as fractions, with the sign of equality in the middle. Perhaps there it is the delightfully mechanical process of cross-multiplying that appeals. However that may be, the fact remains that students use this process in season and out, even using it, and frequently incorrectly, in doing things that should be solved by inspection. They are like the engineering student who was so wedded to his pocket slide-rule that when someone asked him suddenly, "What's two times two?" he whipped the slide-rule out, and after a rapid adjustment, read, "Three point nine nine!"

Personally, I think that ratio and proportion was put into the hands of students by the Devil. My objections to the process are twofold. First, a ratio and proportion can be set up in no less than sixteen different ways, half of which are correct and the other half wrong, and it is difficult to tell by inspection whether a given set-up is right or wrong. In the second place, it is necessary to solve for X, and each bit of algebraic juggling done by a student offers one more opportunity for error, and an opportunity all too rarely foregone. This is particularly true owing to the ingenious way in which students manage regularly to get their X into the denominator on the right-hand side.

To illustrate my first point, look at the possibilities:

$\frac{V}{V_2} = \frac{T}{T_2}$	$V : V_2 :: T : T_2$ $V : T :: V_2 : T_2$	$\frac{V}{V_2} = \frac{T_2}{T}$
$\frac{V_2}{V} = \frac{T_2}{T}$	$V_2 : V :: T_2 : T$ $T : V :: T_2 : V_2$	$\frac{V_2}{V} = \frac{T}{T_2}$
$\frac{V}{T} = \frac{V_2}{T_2}$	$T : T_2 :: V : V_2$ $V_2 : T_2 :: V : T$	$\frac{V}{T} = \frac{T_2}{V_2}$
$\frac{T}{V} = \frac{T_2}{V_2}$	$T_2 : T :: V_2 : V$ $T_2 : V_2 :: T : V$	$\frac{T}{V} = \frac{V_2}{T_2}$
$\frac{T}{T_2} = \frac{V}{V_2}$	$V_2 : V :: T : T_2$ $T : V :: V_2 : T_2$	$\frac{T}{T_2} = \frac{V_2}{V}$
$\frac{T_2}{T} = \frac{V_2}{V}$	$V : V_2 :: T_2 : T$ $V : T :: T_2 : V_2$	$\frac{T_2}{T} = \frac{V}{V_2}$
$\frac{V_2}{T_2} = \frac{V}{T}$	$T_2 : T :: V : V_2$ $T_2 : V_2 :: V : T$	$\frac{V_2}{T_2} = \frac{T}{V}$
$\frac{T_2}{V_2} = \frac{T}{V}$	$T : T_2 :: V_2 : V$ $V_2 : T_2 :: T : V$	$\frac{T_2}{V_2} = \frac{V}{T}$

To make the case easier I have chosen a case of direct proportion, but remember that gas law problems have an equal number of inverse proportions. Furthermore, students rarely label their figures. I wonder how many of you have by this time seen that all of the eight different equations on the left are correct, and those on the right wrong. Of the statements in the center, the upper eight are correct, the lower eight wrong.

Faced with a statement from a student which may be in any one of this multiplicity of forms, even the instructor finds it difficult, as I have said, to tell by inspection whether it is one of the correct forms or one of the incorrect ones. Usually he must repeat in his mind the reasoning process involved in the original writing. The student definitely cannot tell anything by inspection, and if he endeavors to check his work by repeating the reasoning process, he inevitably does just

* Presented before the Division of Chemical Education at the ninety-third meeting of the A. C. S., Chapel Hill, North Carolina, April 13, 1937.

exactly that, repeats it right or wrong, by the hypnotic power of the written word.

My second objection to this process hardly needs more than to be stated. You all know from experience how indiscriminately students get correct or incorrect results in solving such set-ups for X, regardless of whether the set-up itself is correct or not. In any case, any unnecessary mathematical process gives an unnecessary chance for error.

The process of solving an equation for X is completely unnecessary in doing ordinary chemical problems, because the thing can be set up already solved for X, and with even less effort than is required to set up a proportion with the X in some more or less inaccessible position. When a problem is set up solved for X there is only one correct way of writing it. Not only that, but it is easy to detect errors by inspection. Consider the following example:

If 10 ml. of 6 N H_2SO_4 is diluted with water and added to an excess of Zn, what will be the volume of the gas liberated, if measured over water at 18°C., with the barometer at 745 mm.?

$$Zn + 2H^+ + SO_4^{--} = Zn^{++} + SO_4^{--} + H_2$$

10 ml. = 0.01 l. of 6 N acid = 0.06 equivalent. 0.06 equivalent = 0.03 mole of H_2SO_4 = 0.03 mole of H_2 = 0.06 × 22,400 ml. of H_2 S.T.P.

Given		*Find*
672 ml. H_2		X ml. H_2
273°A.	•	273 + 18°A.
760 mm.		745–15 mm.

$$X = 672 \text{ ml. } H_2 \times \frac{291°\text{A.}}{273°\text{A.}} \times \frac{760 \text{ mm.}}{730 \text{ mm.}}$$

The student should reason as follows in setting this up, "I want ml. of H_2 for my answer, so I must start out with ml. of H_2. At a higher temperature the volume will be larger, so in multiplying by the ratio of the temperature I put the larger one on top. The volume will also increase when the pressure is decreased, so the ratio of the pressures also goes large side up. Checking, the units of temperature and of pressure cancel out, leaving the fractions pure numbers, so my answer has the dimensions of ml. of H_2, which was what I wanted."

Students brought up on proportion hate to abandon it for the above method, but when persuaded to do so they make far fewer errors. The main objection to this method is from students who wish to substitute values mechanically in an equation. They don't like a method which requires a thoughtful consideration and understanding of the nature of gases, much preferring to parrot a formula. Personally, I consider this objection a very valid recommendation of the method.

THE CONSTRUCTION OF AN INEXPENSIVE CONSTANT TEMPERATURE WATER BATH FOR SOLUBILITY MEASUREMENTS

WILLIAM JACOB KNOX, JR.

Talladega College, Talladega, Alabama

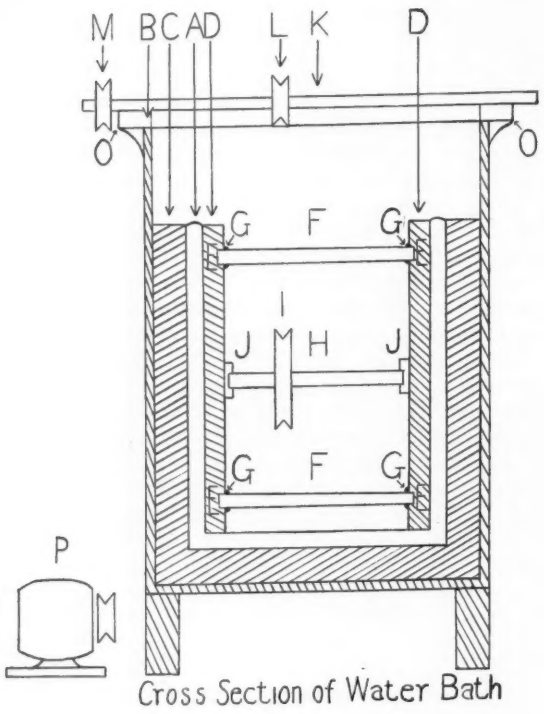
THE high cost of constant temperature water baths of a convenient size for certain types of solubility measurements is often prohibitive for small laboratories. The accompanying diagram shows the vertical cross-section of an inexpensive water bath, useful for such measurements, which can be very easily constructed.

A crock (A), sixteen inches in diameter and twenty-two inches deep, having a capacity of about 70 liters, is placed in a wooden box (B), twenty-four and one-half inches deep, the bottom of which is covered with a solidly packed three-inch layer of finely pulverized pipe lagging. The space between the box and the crock is also solidly packed with finely pulverized pipe lagging. This layer of insulation surrounding the crock is labeled C in the diagram.

Inside the crock is placed two 2 × 4 uprights of white pine (D), each twenty-two inches long and each having been previously soaked in creosote. Each upright is bored half-way through on one of the four-inch faces with two half-inch holes (E) at a distance of about two inches from either end. These holes are fitted with the half-inch brass rods (F). Each rod carries a four-inch thread on either end and is provided with the washers and nuts (G) which when tightened press the uprights against the wall of the crock. This makes possible a very rigid frame for the support of the axle (H). The axle (H) consists of a half-inch brass rod provided with a six-inch grooved, aluminum pulley (I). The ends of the axle terminate in the black walnut bearings (J) fixed at the middle of each upright. Another axle (K) provided with two one-inch grooved, aluminum pulleys (L and M) is supported by the two black walnut bearings (O) screwed to the edges of the box (B) so that the axle (K) lies in the same vertical plane as the axle (H). Directly beneath the pulley (M) is the pulley of the motor (P).

Sample bottles are attached to the axle (H) by means

of large casterloy clamps and clamp holders and are given a rapid end-over-end motion as the motor turns.



The bath is equipped with a Precision Temperature Regulator, Model A and a 600-watt knife-heater. Constant temperatures within 0.1°C. can be obtained.

A RAPID SOLUTION DISPENSING PIPET

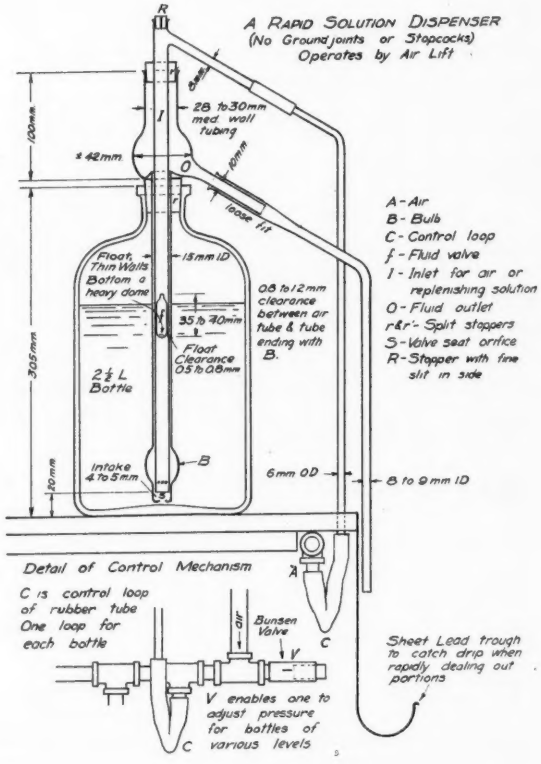
B. J. OTTE, P. J. THOMPSON, AND G. A. BARBER

University of Florida, Gainesville, Florida

THE rapid dispensing of liquid unknowns has always been a problem in most chemistry laboratories. With this in mind the authors set out to make a cheap and fool-proof device. This pipet has been in use at the University of Florida for two years and has cut the time for dispensing our liquid unknowns to about one-third of the former time.

The pipet does not have any ground joints or glass stopcocks and has a rate of flow equal to that of a stopcock with an eight-mm.-bore. Many solutions will cause stopcocks to freeze, and breakage is always high where stopcocks are used. This device lends itself readily to use in multiple units. At present we have eighteen of these connected to the same compressed air line. A bottle of any size may be used.

To facilitate the construction and use of these pipets a few words of explanation are given. The glass from an enclosed porcelain scale thermometer is used to make the float. It is necessary that small vents be placed in stoppers R, r, and r' so that the float may rise as soon as the liquid is dispensed and the liquid is under atmospheric pressure when not in use. The volume of the liquid dispensed is controlled by the size of the bulb B.


A Rapid Solution Dispenser
(No Ground joints or Stopcocks)
Operates by Air Lift
R
r
r'
28 to 30mm med. wall tubing
±42mm
10mm
loose fit
100mm
305mm
Float, Thin Walls Bottom a heavy dome
15mm ID
0.8 to 1.2mm clearance between air tube & tube ending with B.
3.5 to 7.0mm
Float Clearance 0.5 to 0.8mm
2½ L Bottle
Intake 4 to 5mm
10mm
B
6mm OD
8 to 9mm ID
A - Air
B - Bulb
C - Control loop
f - Fluid valve
I - Inlet for air or replenishing solution
O - Fluid outlet
r & r' - Split stoppers
S - Valve seat orifice
R - Stopper with fine slit in side
Detail of Control Mechanism
C is control loop of rubber tube One loop for each bottle
air
Bunsen Valve
V
C
V enables one to adjust pressure for bottles of various levels
Sheet Lead trough to catch drip when rapidly dealing out portions

If stiff rubber tubing is used for the control loop C it is best to tape it loosely so as to make a seal at the bottom, but not so tightly but that by pushing up on the bottom the air may be readily let into the line for dispensing. Pinch clamps may be used, but they are not necessary. It is well to keep all bottles that are connected to the compressed air at approximately the same level. To care for the difference in pressure needed to force the float to the valve seat S a slit is placed in the Bunsen valve V, which is made out of rubber pressure tubing, about eight mm. long. A piece of glass stirring rod is inserted in the tube, and the length of the slit can be varied as needed.

William O. Brooks
A. T. Burtsell
R. K. Carleton
Tenney L. Davis
C. K. Deischer
J. Howard Graham
B. Clifford Hendricks

ABSTRACTS

J. W. Howard
D. C. Lichtenwalner
Greta Oppe

C. M. Pruitt
Leopold Scheflan
A. A. Vernon
E. D. Walter
Mary Elvira Weeks
Sidney Weinhouse
G. H. Woollett

KEEPING UP WITH CHEMISTRY

Radium recovery. Canada's unique chemical industry. M. Pochon. *Chem. & Met. Eng.*, **44**, 362–5 (July, 1937).—Since the discovery of radium many plants for its extraction have been erected and operated, yet essentially their chemical processes follow closely the first procedure used by the Curies in 1898.

In the Great Bear Lake deposits of Northern Canada metallic silver is found strongly associated with the radium-bearing pitchblende. As a result the process is carried out in four steps: (1) the preparation of the minerals by roasting and milling, (2) the recovery of the silver and the reduction of the radium into radium-barium sulfate, (3) finishing of the radium in the laboratory and (4) refining of the uranium salts. The separation of the radium from the barium is effected by fractional crystallization of the water solution of radium and barium bromides. Each crop of crystals is richer in radium and poorer in barium than the liquor above it. The starting liquor has 400,000 parts of barium to one of radium. After twenty-three crystallizations commercial radium bromide containing nine parts of radium to one part barium bromide is finally produced.

Uranium oxide, nitrate, and acetate are also products of this plant. J. W. H.

Recent British research on motor spirit from tar. C. H. S. Tupholme. *Ind. Eng. Chem., News Ed.*, **16**, 221–2 (1938).—Description of experimental plant constructed by the British Fuel Research Board to study the hydrogenation of low-temperature tar. The raw material input is two hundred to four hundred gallons per day and the ratio of hydrogen to oil is two hundred to five hundred cubic feet per gallon. About fifty per cent. by volume of the total feed material or one hundred per cent. by volume of the fresh tar treated is converted to an oil boiling below 200°. This can be used for motor fuel. A. A. V.

Weston-Levine Vitamin Chart. R. E. Remington. *Ind. Eng. Chem., News Ed.*, **16**, 234–5 (1938).—This is a very valuable chart giving names, functions, and sources of vitamins. A copy of the chart may be obtained from Dr. Roe E. Remington, 280 Calhoun Street, Charleston, South Carolina, by forwarding ten cents. A. A. V.

A simple blast burner. F. C. Fair and J. J. Young. *Chemist-Analyst*, **27**, 1, 18 (Jan., 1938).—A 15-mm. test-tube is cut off near the bottom and then closed and discarded. The cut end is heated until it partially closes. Two pieces of 3-mm. glass tubing are inserted into a two-hole rubber stopper and inserted into the end of the test-tube. The air inlet should extend almost to the open end of the test-tube, but the gas inlet should end several millimeters above the stopper. A clamp can be used to hold it in position. This burner has been used successfully for limestone ignitions. D. C. L.

Producing natural soda ash in Washington. J. D. Lindsay. *Chem. & Met. Eng.*, **45**, 144–5 (Mar., 1938).—A plant has been installed at Wilson Creek, about one hundred miles west of Spokane, Washington, for the production of soda ash from a natural deposit. The deposit is in the form of a lake occupying thirteen acres lying between two rather high lava formations. Drillings have been made to a depth of fifty feet and still show good values. The deposit is rather pure sodium carbonate mixed with some insoluble silt.

The process used dissolves the sodium carbonate from the bed, and after separating any insoluble matter, crystallizes, dries, and granulates it into soda ash. J. W. H.

Stream pollution becomes a problem for chemical engineers. Editorial Staff. *Chem. & Met. Eng.*, **45**, 138–9 (Mar., 1938).—Prevention of stream pollution has become a chemical engineering problem quite as much as one of sanitary engineering importance. Process industry throughout the country is finding it necessary to make extensive investigations and frequently to install costly effluent disposal works in order to prevent the contamination of streams. Both the public and the industry benefits by the purer water supply.

Contamination of waterways is more frequently occasioned by municipal sewage discharge than by industrial wastes, it being estimated that the sewage of 40,000,000 people is discharged into streams without treatment. In cases where the plant effluent goes into a municipal sewer system there are important problems involved in the effect of the effluent on sewage disposal.

Industries are now spending large sums for pretreatment of the effluent from their plants and feel municipalities should do likewise with respect to sewage discharge. J. W. H.

High pressure blast. Anon. *Ind. Bull. of Arthur D. Little, Inc.*, **134**, 1 (Mar., 1938).—It is pointed out here that the blast furnace might increase its capacity and improve its efficiency if a reducing gas, such as surplus coke oven gas or producer gas, were introduced at some intermediate point of the furnace shaft to increase the reducing capacity of the gases in the reduction of iron ore. G. O.

PROFESSIONAL

The manufacture of neon signs. W. J. Clancy. *Rept. New Eng. Assoc. Chem. Teachers*, **39**, 32–5 (Sept., 1937).—Students display an interest in neon sign lighting, and a discussion is interesting in both physics and chemistry classes. Three kinds of inert gases are used: neon, argon, and helium. In addition, mercury vapor is employed to get some of the color effects. The inert gases are shipped to the manufacturers in glass liter flasks fitted with a clever device to permit removal of the gas without contamination with air. The cost of the inert gases, spectroscopically pure, is about $9.00 a liter at atmospheric pressure. Mercury vapor is obtained by heating mercury over a cup-like electric furnace. The different colors are obtained by using different combinations of colored glass tubing with different gases. A mixture of neon, argon, and mercury vapor gives a blue light in clear tubing, a white light in milk-white glass, and a green light in a yellow tubing. Neon gives an orange-red color in clear tubing and a deep red color in a ruby-colored glass tubing. A variety of colors is possible by using different combinations of gases and colored glass tubing. The tubing used is commonly from 4 mm. to 10 mm. inside diameter and is received by the manufacturer in four-foot lengths. Glass blowers bend the glass to form the desired letters and weld the lengths of tubing together as needed. A high vacuum is secured within the tube and then a low pressure of the inert gas is admitted. Neon signs usually have a pressure

of 6 to 16 mm. of gas, while helium is used in the signs at about 4 mm. pressure. A transformer is used to raise the voltage from 110 to a high voltage that varies from 2000 to 15,000, depending upon the length and internal diameter of the tubing.

W. O. B.

FOREIGN CHEMICAL AND EDUCATIONAL CONDITIONS

Italian chemical industry turns to autarchy. EDITORIAL STAFF. *Chem. & Met. Eng.*, **45**, 124–5 (Mar., 1938).—The information for this article was obtained through an interview with Dr. Ing. Giacomo Fauser, famous chemical engineer of Italy.

In Italy the chemical industry is closely controlled and carefully guided by the State under the Central Corporative Committee. It is forced to adopt an autarchy, substituting domestic products for imports wherever possible. This greatly stimulates research and technical development. Since so much of her gasoline must be imported, all gasoline is now mixed with twenty per cent. fuel alcohol, about ninety-eight per cent. of this alcohol coming from sugar beets. Hydrogenation of fuels is also advancing rapidly.

Fertilizers are being used in increasing amounts with gratifying results. The nitrogen industry of the country supplies all of its needs. There are plants for making both synthetic ammonia and cyanamide. Fifty-five per cent. of the hydrogen needed for synthesis is prepared by electrolysis, the rest from coke ovens. Potash is imported from Germany and phosphates are made from North African phosphate rock.

While chamber installations are still in preponderance there is an increasing trend toward making H_2SO_4 by the contact method. A large tonnage is made as a by-product of one of the big zinc smelters. Italy has plenty of pyrites and brimstone.

Production of aluminum is expected to reach 30,000 tons annually in the near future.

J. W. H.

Canadian emanations. ANON. *Ind. Bull. of Arthur D. Little, Inc.*, **126**, 3–4 (July, 1937).—In 1930 in the remote fastnesses of the Canadian Northwest, a prospector, skirting the shores of Great Bear Lake, came upon a rich deposit of copper, cobalt, silver, and lead, with smaller amounts of manganese and iron, and transcending in importance all of these, pitchblende, the much-sought uranium-bearing ore from which precious radium is recovered. This event was epochal in its significance to the Canadian chemical industry and to the works scale production of radium in the New World. Three years later active work began on the production of radium under the direction of Dr. M. L. Ponchon who is said to be the last survivor of the little band of chemists associated in the hazardous and difficult work, radium isolation, led by Madame Curie. Prior to the Canadian production, the price of radium was controlled at $70,000 per gram by a Belgian company operating in the Belgian Congo. The current market price is $30,000 per gram or approximately $850,000 per ounce avoirdupois. Production in Canada at the end of the third year of operation amounted to approximately one ounce avoirdupois of purified radium bromide, which represents the working of some three hundred tons of ore. It is hoped to increase the yearly capacity to three ounces. From a ton of pitchblende the average yield of the purified radium bromide is equivalent to the "amount of salt one would sprinkle sparingly on an egg". In the course of the separation and isolation of the radium a staff of trained chemists is required because of the highly specialized technic required, together with the increasing hazard to the operators.

G. O.

GENERAL

Advances in botany. F. E. DENNY. *Ind. Eng. Chem., News Ed.*, **16**, 1, 3–4 (Jan. 10, 1938).—The following are of interest from the chemical viewpoint. Cobalt was shown to be an important factor in control of certain sheep diseases. Co content was 0.2 P.P.M. in forage crops where sickness was produced while recovery occurred when the Co content was 0.45 P.P.M. Treatment of the soil with limonite which contains Co caused recovery. Frenching, a disease of tobacco is believed to be caused by thallium; 0.067 P.P.M. produces the symptoms of the disease. Nitrogen fertilizers, $Al_2(SO_4)_3$ and KI, overcome the disease.

Cauliflower browning, cracked stems of celery, and yellowing of alfalfa are due to boron deficiency. Soil organisms sometimes rob plants of their necessary Mn or Zn requirements. This can be overcome by sterilizing the soil or adding extra Mn for oats or Zn for peaches. Work on the influence of vitamin B_1 and related substances on plant growth are reported. Proteins previously isolated which possessed the properties of the tobacco mosaic were found to have a molecular weight of 10,000,000 while in healthy plants the highest value was 30,000. Field tests for identification of plant viruses have been developed. Measurements of the rate of photosynthesis and respiration in plants have been carried out by the spectrophotographic method under varying degrees of illumination. Respiration seems to be unaffected by light.

Radioactive phosphorus has been utilized to study rate of movement within the plant. It moves about 23 cm. in forty hours, moving nearly as fast in the bark as in the wood and pith. Certain cells when placed in deuterium oxide or heavy water show removal of water from the cell. Certain marine algae were reported which had a pH of 0.78 and total acidity of 0.425 *N* in the plant juices. Cl and SO_4 content were high, only a trace of organic acids were present, so that figured as H_2SO_4, twenty-one per cent. of the plant was H_2SO_4.

D. C. L.

Handwriting on the wire. ANON. *Ind. Bull. of Arthur D. Little, Inc.*, **134**, 3–4 (Mar., 1938).—Facsimile messages and pictures have been flashed across the Atlantic by both radio and cable. Experiments in transmission between Tokyo and San Francisco are in progress, and "picture telegram" services are in transmission in Europe. In the United States Western Union offers such service at New York, Buffalo, and Chicago. This is an interchange of line drawings, blueprint designs, tabulations, handwritten or typed manuscripts, advertisements, or printed matter. The Western Union is now using a new, dry facsimile receiving paper developed to record by direct electrical action, yet is not sensitive to light or atmospheric conditions, and is ready for delivery as it comes from the machine. There are also private facsimile systems. Matter to be transmitted by facsimile usually is fastened to a metal cylinder revolved before an electric eye. Simultaneously, a beam of light is focused on the revolving cylinder, providing controlled illumination to be absorbed in dark portions or reflected to the electric eye by light parts, the variations of intensity of this reflected light producing corresponding electrical impulses which are then amplified and sent over telegraph lines or by radio to the distant recorder. At the other end recording paper and a stylus or photographic paper and a beam of light trace the facsimile.

G. O.

America revisited. G. W. C. KAYE. *Nature*, **141**, 495–8 (Mar. 19, 1938).—During his recent trip to the United States and Canada, Dr. Kaye visited many great research centers, including the University of California, where "E. O. Lawrence by his genius and persistency has developed the cyclotron into the most potent practical contribution of recent times to the study of neutrons and artificial radioactivity"; Leland Stanford University with its two-million-volt transformer; the California Institute of Technology, where he observed Dr. C. C. Lauritsen's work on supervoltage X-ray therapy, and the grinding of a 200-inch reflector; and Chicago, where he attended the Fifth International Congress of Radiology. He states that the cyclotron has given "the biological worker and radiologist two powerful new tools, in the shape of artificial radioactive elements and neutrons. Some twenty-five outfits are at present under construction the world over, six or seven in the States and two in England (Cambridge and Liverpool). . . Both in Berkeley and elsewhere the study of neutron therapy (on animals) is being taken up. Neutrons ionize in a manner very different from that of gamma or X-rays, and are unique in being more absorbable in body tissue than in bone. If the present claims of selective reaction to tumor tissue are substantiated, it would seem that neutrons may presently have high therapeutic significance."

M. E. W.

RECENT BOOKS

ORGANIC CHEMISTRY, an advanced treatise. *Henry Gilman, Editor*, Iowa State College, Ames, Iowa. John Wiley & Sons, Inc., New York City, 1938, 2 vols. Vol. I, lvi + 858 pp.; Vol. II, lvi + 1032 pp. 15 × 23 cm. $7.50 per volume. Available separately.

The present volumes are the result of the combined efforts of numerous specialists in the several branches of organic chemistry. Each author has prepared a chapter dealing with a subject of particular interest to himself. "It was hoped to obtain, in this way," according to the editor, "an authoritative treatise which would cover most of the important phases of organic chemistry." The treatment does not claim to cover the simple fundamental items that are adequately discussed in numerous and excellent elementary textbooks. These two volumes are designed for instruction at the graduate level. The emphasis has definitely been placed upon new developments.

The wide range of important material included and the ability of the several authors can best be realized by a perusal of the table of contents. Volume I contains the following chapters: Alicyclic Compounds and the Theory of Strain, Reynold C. Fuson, University of Illinois; Theory of the Structure and Reactions of Aromatic Compounds, Louis F. Fieser, Harvard University; Stereoisomerism, R. L. Shriner, Roger Adams, and C. S. Marvel, all at the University of Illinois; Organometallic Compounds, Henry Gilman, Iowa State College; Free Radicals, Werner E. Bachmann, University of Michigan; Unsaturation and Conjugation, C. F. H. Allen, Eastman Kodak Company, and A. H. Blatt, Howard University; Open-Chain Nitrogen Compounds, Charles D. Hurd, Northwestern University; Molecular Rearrangements, Everett S. Wallis, Princeton University; and Comparison of Chemical Reactivity, Homer Adkins, University of Wisconsin. Volume II includes the following chapters: Natural Amino Acids, H. T. Clarke, Columbia University; The Chemistry of Pyrimidines, Purines, and Nucleic Acids, Treat B. Johnson, Yale University; Alkaloids, Lyndon F. Small, University of Virginia; The Anthocyanins and the Flavones, Karl Paul Link, University of Wisconsin; Carotenoids: the Polyene Pigments of Plants and Animals, Marston Taylor Bogert, Columbia University; The Sterols, Bile Acids and Related Compounds, William H. Strain, School of Medicine and Dentistry, The University of Rochester; Carbohydrates I, Melville L. Wolfrom, The Ohio State University; Carbohydrates II, Albert L. Raymond, G. D. Searle & Co., Chicago; Carbohydrates III—Cellulose, Emil Heuser, The Institute of Paper Chemistry; Modern Electronic Concepts of Valence, John R. Johnson, Cornell University; Constitution and Physical Properties of Organic Compounds, Wallace R. Brode, The Ohio State University, and John A. Leermakers, Eastman Kodak Company; Rotatory Dispersion, P. A. Levene and Alexandre Rothen, both at the Rockefeller Institute for Medical Research; and The Significance of Resonance to the Nature of the Chemical Bond and the Structure of Molecules, Linus Pauling, California Institute of Technology.

It will be noted that the chapters dealing with natural products, relationship between physical properties and chemical constitution, valence, and resonance have been grouped together in the second volume. Topics of a more nearly standardized nature have been grouped together in Volume I. This will aid materially in subsequent revising and expanding of the books. The reviewer is glad to note that such future revisions are already contemplated to keep these volumes systematically up to date, by even the inclusion of new chapters to fill the more conspicuous gaps. "For example, chapters on polymerization and chlorophyll will be included in the next edition."

In spite of the fact that these books have been prepared by twenty-seven different authors, the contents have been conveniently integrated and correlated by numerous cross references. Individual tables of contents have been added for each chapter. A very comprehensive subject index to the two volumes is included in each of the two books. References to the original literature are necessarily limited, and yet those references selected are, as a rule, to the most recent publications, or to articles that lend an historical background, or offer numerous other lead references to the literature. In many instances the references have been brought up to September, 1937. The General References at the end of each chapter include many of the more important review articles and books as a guide to collateral reading.

These books are neatly and substantially bound. The printing is clear and attractive. The volumes are profusely illustrated with apt drawings where such illustrations are needed. The text is remarkably free from typographical errors. For one man to criticize adversely, if such was possible, such a work, which represents the combined efforts of such an impressive list of contributors, would verge on the presumptuous. Suffice it to say that these two volumes represent what is perhaps the greatest similar American contribution to organic chemistry. One is impressed with the vast amount of splendid material and the unusual quality of these two volumes. They are indispensable to every chemist, whether in teaching, graduate work, or practicing in the field.

RALPH E. DUNBAR

NORTH DAKOTA AGRICULTURAL COLLEGE
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GENERAL CHEMISTRY FOR COLLEGE STUDENTS. *George Washington Muhleman*, D.Sc., Editor, Professor of Chemistry at Hamline University, and five other authors. Burgess Publishing Company, Minneapolis, Minnesota, 1937. iv + 270 pp. 20 × 28 cm. $2.75.

This is a mimeoprinted text which is to be revised each year. The six joint authors are situated in five different colleges and universities. They think that current textbooks in general chemistry differ too much in content and in methods of treatment, and they have attempted to correct this difficulty by conferring and counseling together in regard to their own textbook. The introduction states, "This textbook has been written by different authors who have been eminently successful as teachers and who understand the student mind and the way it learns." . . . "By pooling their experiences as teachers in one text and in thus sharing their methods of presentation, the student has the advantage of learning his general chemistry not from one teacher alone but from many teachers."

The opening chapters deal with the nature of matter, the structure of the atom, oxygen, hydrogen, and valence. The first one hundred forty-three pages are called the theoretical part, but they include also the descriptive treatment of halogens, atmosphere, nitrogen and nitro en compounds, sulfur, selenium, and tellurium. The descriptive part contains ninety-four pages devoted to the most common elements and a chapter on electrochemistry. Many of the less common elements are not mentioned at all. The alkali metals are disposed of in less than two pages, the explanation being that by the time the student has arrived at this stage he has already become acquainted with most of the compounds of these elements because of his work with them in the laboratory, and—as is recommended elsewhere—because of his reading in the library.

The book appears to be an outline which is to be supplemented by a considerable amount of material from other sources. The manner of treatment is conventional. No mention is made of modern conceptions of acids and bases, ionization, or metals.

E. A. WILDMAN

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GENERAL AND INORGANIC CHEMISTRY. *Frederick C. Irwin*, B.S., Professor of Chemistry, and *G. Ray Sherwood*, Ph.D., Assistant Professor of Chemistry, Wayne University. Fifth Revised Edition. Lithoprinted by Edwards Brothers, Inc. Ann Arbor, Michigan. ix + 626 pp. 92 figs. 13 × 22 cm. $3.85.

This book is a revision of an earlier text, GENERAL CHEMISTRY FOR COLLEGES. The present edition, so the preface states, consists of Part I which "tries to place most emphasis upon contributions of chemistry toward a general education"; while Part II "is practically all devoted to inorganic chemistry" because most of "the students who study this will continue with qualitative analysis."

The division of the book is not so clear cut as might be imagined. The table of contents shows that Chapter XIX is a Review and Summary, but there is nothing else to indicate that Part II begins with Chapter XX (Oxygen Compounds of the Halogens).

In the first eighteen chapters there are seven chapters (nonconsecutive) devoted to theory. These are brief, but ample and well written. This portion of the text proceeds logically to develop the chemistry of oxygen, hydrogen, water and solutions, chlorine, the halogen family, carbon, and also contains four chapters devoted to organic chemistry.

The latter part of the book contains chapters relating to oxygen compounds of halogens (introduced perhaps rather late), solutions considered quantitatively, laws of electrolysis, sulfur, its oxides, etc., nitrogen, inert gases, phosphorus, arsenic, antimony, and bismuth. Chapter XXVII reviews fundamental principles of physics. Chapter XXIX is a short treatise of X-ray spectra and crystal structure. Chapter XXXII is a further development of the periodic system, first treated in Chapter VIII. Chapters XXXIII to XL are devoted to the metals. The concluding Chapter (XLI) is an interesting survey of colloids.

There is good historical introduction to the subjects considered. References to source material are scanty. In most cases only the essence of required theory is included. For a book which succeeds so well in general it is surprising to find occasionally such detailed instructions as those on page 117 where the instructions for the preparation of HCl sound like a laboratory manual.

Owing to the method of lithoprinting there are the usual shortcomings of this style. Some pages are printed in light type unintentionally, most in uniform heavier type. Diagrams are not too well done. Some pages of the book reviewed are slightly smudged. There is only one good photograph reproduced and only a few more attempted.

Physiological explanations of chemical processes are well explained. The style is easy and the subject matter clarified for the beginner. What the book lacks in attractiveness is largely compensated by concise treatment. One fancies the authors drawing freely from their lecture notes.

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THE TEACHING OF PHYSICAL SCIENCES IN THE SECONDARY SCHOOLS OF THE UNITED STATES, FRANCE AND SOVIET RUSSIA. *Alexander Effron*, Ph.D. Bureau of Publications, Teachers College, Columbia University. Contributions to Education, No. 725. New York City, 1937. vii + 296. 15 × 23 cm. $2.35.

This thesis is based on a seven-month resident study in France and Russia and fifteen years of experience in teaching physics in New York high schools. The author compares "the content and organization of the course of study, the training of science teachers, the nature of tests and examinations, the character of textbooks, the methodology of science teaching, the conduct of extracurricular science work, and the design and utilization of science equipment." Under these several headings he discusses the teaching of each physics and chemistry in the United States (ninety pages), France (seventy-nine pages), Russia (seventy-two pages). Then follows an interpretative summary (twenty pages) and his conclusions and implications (three pages). There is included also a comparison of the systems of secondary education in the three countries. Throughout are frequent quotations from the literature, two hundred forty-one titles, in the bibliography.

He saw thirty-six lessons given in France, twenty-one in Russia. He gives his notes on five (three chemistry) observed in the United States, seven (three chemistry) in France, six (one chemistry) in Russia. One is disappointed to find so little space (eight pages) devoted to recording the raw data on which so many of his judgments must be based. And these include little of pupil activity. Here is an abbreviated sample: Chemistry, twenty-four boys who were from fourteen to fifteen years old. Laboratory well equipped, light, airy, conveniently arranged. Individual work. Four separate experiments attempted. Both teacher and laboratory assistant busy, suggesting, assisting, and criticizing procedure. Records entered carefully and neatly (page 175).

One should obtain from reading the thesis a fairly clear idea of the teaching of these subjects in the three countries in so far as New York City and vicinity, Paris, Leningrad, and Moscow are typically representative. A few of his statements are misleading. "The French secondary school proper is not based on the primary school" (page 102). But surely no pupil gets into the secondary school who has not completed the course in a primary school (or elementary) and successfully passed its promotional examination.

He asserts that the New York State Regents syllabus and the College Entrance Examination Board syllabus are probably the most important factors in determining the curriculum content in these subjects. (Are the Appalachians his horizon?) These he gives and similar courses of French and Russian schools. Teachers in French secondary schools are better trained in subject matter than in the United States but not so well versed in pedagogy. Textbooks here are mechanically superior to those in use in the countries he visited. These are just samples of the comparisons he makes.

As a result of his study he has little to offer in the way of improving the teaching of the physical sciences in the United States. He does think we might copy with profit "the French emphasis on clarity of expression and care in oral and written expression" and the Russian correlation of the extracurricular science program with the work of shops, factories, power plants, and collective farms.

ELLIOT R. DOWNING

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VAN NOSTRAND'S SCIENTIFIC ENCYCLOPEDIA. D. Van Nostrand Company, Inc., New York City, 1938, 234 pp. 19 × 27 cm. $10.00.

This book contains in one large volume essential facts from the fields of aeronautics, astronomy, botany, chemistry, engineering, geology, mathematics, medicine, mineralogy, navigation, physics, and zoölogy. A group of professors from well-known colleges and engineering schools compiled the book. The policy adopted was to have one man responsible for the articles on his specialty. He was assisted by competent scientists and aided by still others as consultants. The list of Contributing Editors and Consulting Editors is given in the frontispiece and each article in the book has appended the initials of the person who contributed it. The authors are men of unquestioned standing in their respective fields. The Contributing Editor for Chemistry is Dr. Ralph K. Strong, Professor of Chemistry at Rose Polytechnic Institute and the Consulting Editor, Dr. Hugh S. Taylor, Research Professor of Chemistry at Princeton University. The subject matter is up to date (some information is actually dated 1938) and authoritative.

The subjects are arranged alphabetically with the names of the subjects printed in bold-face type, which facilitates the use of the book. Over 10,000 terms are explained (some take more than a page and some just a few lines) and the system of cross-references makes it easy to find material under different headings. The policy of the book is to present a progressive development of the discussion of a topic from simple terms in the early portion of an article to more detailed consideration in later portions. The

book thus serves the inquiring layman or a trained technician. More than 1200 line-drawings and half-tones are used to illustrate the book. The printing is clear, the binding is strong, and the appearance of the book is attractive.

The chief fault of the book is that one volume cannot contain all the information on so many branches of science. The authors were forced to limit the subject matter to prevent unwieldy size. Few of the great men of science are mentioned. The book should not be used in place of Standard Tables as many of the boiling points and freezing points, for example, have been rounded-off. Pronunciations are not given.

The material on aeronautics is comprehensive and much of it is novel to the average science teacher. In addition to the basic sciences the material under the applied sciences of navigation, medicine, and the various branches of engineering furnishes information frequently needed but not readily available, at least, not all in one volume. Such subjects as *brickwork, types of bolts, burns of flesh, lubrication, steam condensers, locomotives, metal stamping, wind-tunnels, refrigerants, Great Circle course,* and *headaches* are typical of hundreds of articles which I found described in an interesting and informative manner. The articles on *television, satellites, power generation,* and *human blood* are notably good.

Features that appealed to me as a chemistry teacher were: (1) the excellent articles on each element; (2) the history and evolution of chemistry; (3) the hydrogen-ion chart; (4) descriptions of important dyes; (5) the material on sulfuric acid; (6) the profusion of material on organic chemistry; (7) the wealth of material on water and water analysis; and (8) the articles on catalysis, solvents, hydrocarbons, and filtration equipment.

It is impossible to give an adequate picture in a short review of such a comprehensive book. I think the book is valuable for the private library of every scientific person and should be available in all school and public libraries.

WILLIAM O. BROOKS

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MICROMETHODS OF QUANTITATIVE ORGANIC ELEMENTARY ANALYSIS. *Joseph B. Niederl,* Ph.D., Assistant Professor of Chemistry and *Victor Niederl,* Teaching Fellow; New York University, Washington Square College. John Wiley and Sons, Inc., New York City, 1938. xvi + 271 pp. 53 figs. 14.5 × 23 cm.

A few quotations from the preface will give the authors' purpose. "This book is primarily a laboratory manual for teaching and practicing the methods of quantitative organic microanalysis of pure organic compounds under ordinary laboratory conditions and is intended principally for colleges giving a course in this subject and for organic chemical research laboratories, either industrial or academic."

"In teaching these methods. . . .F. Pregl's book DIE QUANTITATIVE ORGANISCHE MIKROANALYSE, as well as its subsequent English translation, were first used. . .however, it appeared desirable to introduce certain changes, so that chemistry students without previous training in microchemical technic, as well as chemical laboratory technicians, could follow the procedures. In accordance with this viewpoint, shortened and concise working procedures were prepared in the form of mimeographed outlines. These outlines were revised each year until they reached the form presented in this book. . . .It was necessary to adapt the various procedures to ordinary laboratory conditions without impairing their intrinsic value and accuracy; furthermore, they had to be simplified to make them comprehensible to a rather large number of students possessing only an average undergraduate knowledge of chemistry."

The contents follow: *Introduction.* The Microchemical Balance, Weighing on a Microchemical Balance, Miscellaneous Weighing Equipment, Miscellaneous Laboratory Utensils, Preparation and Weighing of a Sample. *Elementary Analysis.* Metals and Residues. Neutralization Equivalent, Volumetric Aminoid Nitrogen, Gasometric Nitrogen, Carbon and Hydrogen, Halogens, Sulfur, Phosphorus, Arsenic. *Molecular Weight.* Ebullioscopic, Cryoscopic, Vaporimetric and Osmotic Methods. *Structure Analysis.* Alkoxy and Alkimide Groups, Acetyl Groups, Active Hydrogen. *Appendix.* The Teaching of Quantitative Elementary Organic Microanalysis, Installation of a Laboratory, General Microchemical Literature, Calculations and Tables.

As described in the preface, this book was developed during ten years' experience in teaching the Pregl methods as a special course in the Graduate School at New York University. Before this course was introduced into the curriculum, Professor Niederl was well known for his interest in the Pregl methods and for his work abroad and in New York. Using Professor Pregl's original procedures as a background, Niederl has drawn freely from the literature and his own experience in preparing this laboratory manual. Each method has been used by a large number of students under critical supervision. Many literature citations are given at the end of each section, each one of which is mentioned or discussed.

Professor Niederl has made a most valuable contribution to chemical education and research in presenting in such an attractive form the best microchemical methods for quantitative organic analysis.

This manual will no doubt take its place as a standard work for all teachers and investigators interested in microchemical methods for organic analysis.

RALPH T. K. CORNWELL

SYLVANIA INDUSTRIAL CORPORATION
FREDERICKSBURG, VIRGINIA

SCRIPTA MATHEMATICA FORUM LECTURES. *Cassius Jackson Keyser, David Eugene Smith, Edward Kasner, and Walter Rautenstrauch.* Yeshiva College, New York City, 1937. iii + 94 pp. 8 figs. 12 × 20 cm. $1.00.

The small volume contains four interesting addresses. The first one, entitled "Mind, the Maker," by Cassius Jackson Keyser, Adrain Professor Emeritus of Mathematics in Columbia University, gives a summary of "The World Theory of the Late William Benjamin Smith." The scientists, dealing with a "Universe of Measures and Measurables," one of "Signs and Symbols," propose and answer the sole question *How.* The author believes that to answer the query *Why* is equally important. Thus, the address deals with what may be designated, in a nonderogatory manner, as metaphysics. What is *Reality?* It is the problem which philosophers have attacked since the time of Plato, with ever the same result.

The address emphasizes once more the fundamental difference between the two methods of interpreting the universe about us: the scientific, experimental, and the intellectual, cogitational. While the reviewer confesses to a lack of sympathy for the latter method, Professor Keyser's address is certainly thought-provoking.

The second address on "The Story of Mathematics," by David Eugene Smith, Professor Emeritus of Mathematics in Columbia University, compresses in nineteen stimulating pages a topic upon which many volumes have been written.

"New Names in Mathematics," by Edward Kasner, Adrain Professor of Mathematics in Columbia University, deals with "new words, new terms, in more or less recent mathematics." As the author points out, "We cannot get along without new names as we advance in science. We need new names for new ideas and new forms. A peculiar thing about mathematics is that it does not use so many long and hard names as the other sciences do. Chemistry, physics, and biology employ tremendously long names. In mathematics we use many easy words: 'group,' 'family,' 'ring,' 'simple curve.' But these ordinary words of English are given a very peculiar and difficult technical meaning. In fact, here is a booby prize definition for mathematics: *mathematics is the science which uses easy words for hard ideas.* In this it differs from any other science."

To the terms such as those mentioned above, the author adds some new ones. For instance, a *cycle* is a circle with an arrow on

it, indicating direction of rotation. The equation of the fifth degree cannot be solved with radicals, but in terms of algebraic functions to which the author gives the name "ultra-radicals." What is a very large number? The author chooses a "googol" which is 10^{100}, and states, "The reason that I have given a name to this particular number is that it is just larger than the largest numbers that are used in physics or astronomy." A still greater number is a "googolplex" which is $10^{10^{100}}$. It would be impossible to write down all the zeros "even if you went to the farthest star, putting down zeros all the way there and making a tour of all the nebulae."

The last essay in the volume is "Science in Relation to Social Growth and Economic Development," by Walter Rautenstrauch, Professor of Industrial Engineering in Columbia University. The author points out that growth in general is characterized by two coincident developments which are: "1. The appearance of new functions and functional mechanisms. 2. The extension of their integrating and coördinating systems." Science and engineering have provided society with a vast number of technological advances, but for lack of proper coöperation between engineer and economist, social growth has not kept pace with technical developments. The author therefore formulates certain principles by means of which the social structure may be "redesigned along scientific lines." Perhaps in the dim future when humanity has learned some more lessons at the cost of much suffering, such suggestions will bear fruit.

SAUL DUSHMAN

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PRINCIPLES OF POWDER METALLURGY, with an Account of Industrial Practice. *W. D. Jones*, Sir John Cass Technical Institute. Longmans, Green and Company, New York City, 1937. xii + 199 pp. 73 figs. 13.5 × 21.5 cm. $5.00.

This is the first book on this subject that has appeared in English. This fact, however, is indicative of recent rapid development, rather than of any lack of importance, of this branch of metallurgy.

Powder metallurgy, or metal ceramics as it is sometimes called, has to do with the preparation of metal articles, or compacts, by sintering of a compressed metal powder. The first part of the book is concerned with the physics and chemistry of sintering. The author does not consider sintering to be predicated on partial fusion of the particles of solids; he suggests in fact that fritting be used to describe the condition in which liquid phase is present. The actual forces that effect sintering are normal surface cohesive forces of the metal. Since these forces decrease with temperature, how, then, one may ask, is it possible for cohesion to increase with temperature? The answer is that increase in temperature causes the metal to become more plastic, so that a greater area of contact of the particles is effected. Pressure also acts by the plastic flow which it causes.

Having emphasized the importance of surface cohesive forces, the author is led naturally to consider oxide and other surface films, and the removal of such films by mechanical and chemical means.

Physical factors of particle size, size distribution, and shape are given due consideration. These factors determine the degree of contact between particles and so affect the porosity, shrinkage, and mechanical strength of the compact.

Intercrystalline impurities, grain growth, recrystallization, age hardening, and diffusion in polymetallic compacts, are little understood in their relation to powder metallurgy, and these topics are not more than touched upon. On the other hand, fairly lengthy but interesting experimental details are provided on the subjects of mechanical properties, electrical conductivity, and permanence of metal compacts.

The last half of the book is concerned with a description of the manufacture by sintering of hard metal compacts, hard metal alloys, and with the preparation, properties, and testing of metal powders. Probably the most important product of today is the so-called oilless bronze bearing, a porous composition of copper and tin that is impregnated with oil, and one which finds much use in the automotive industry. Other manufactures described include iron, nickel, and their alloys, chromium, and tungsten, as well as other metals. The hard metal alloys include tungsten carbide, the carbides of tantalum, titanium, and molybdenum, and mixtures of these. The methods of preparation of metal powders are varied and may be enumerated as follows: deposition from a gas (carbonyl powders), electrolytic deposition, mechanical comminution, and to a lesser extent precipitation and atomization.

The book covers its subject well and possesses numerous references and a good index. The author has attempted to place the subject on a firm foundation of principle, but is commendably cautious. The treatment is on the whole critical but is fair in presenting other points of view. In showing where knowledge of the subject is inadequate, useful suggestions for further research have been made. The book should prove instructive and stimulating not only to the specialists in powder metallurgy, but also to the reader with a general interest in this developing field.

PAUL S. ROLLER

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AN ELEMENTARY COURSE IN QUALITATIVE ANALYSIS. *William Lloyd Evans, Jesse Erwin Day,* and *Alfred Benjamin Garrett,* The Ohio State University. Ginn and Company, New York City, 1938. vii + 234 pp. 17 figs. 20 × 26 cm. $2.00.

By the statement of the authors this book is designed for the student of elementary qualitative analysis. In the opinion of the reviewer the authors have attained extraordinary success in accomplishing their stated purpose. The first few pages of the book are taken up with some introductory remarks and a description of some simple apparatus and laboratory operations. The cations are treated on pages 13–105 and the anions on pages 111–45. The cations are divided into the usual five groups. The separation of the cations are brought about by the use of what might be termed as orthodox reagents and methods. The confirmatory tests are in the main those that have been found to be satisfactory for many years. A few of the newer tests that have been found to be satisfactory are included, such, for example, as the use of uranyl acetate for the sodium test. The use of organic reagents is deliberately avoided with one or two exceptions, *e. g.*, dimethylglyoxime is used in testing for nickel. Micro procedures are deliberately avoided for which the authors should be warmly commended. Numerous preliminary tests with appropriate chemical reactions precede the laboratory directions for the analysis of each group, which directions, given in the form of block outlines, are accompanied by notes and flow diagrams and are followed by review questions and laboratory record sheets. The anions are treated in the same general way in so far as the analysis of the anions permits. The last part of the book is taken up with the theory of qualitative analysis and appendixes which contain much valuable information. The book is printed in clear, unusually readable type and is bound loose-leaf style with a thin cardboard back. A book of this quality deserves a better binding. Of the many qualitative laboratory manuals that have been published in the last several years this one should without doubt be rated near the top so far as its general usefulness to the student is concerned.

LYMAN J. WOOD

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By J. H. REEDY, University of Illinois. *International Chemical Series.* In press—ready in September.

The purpose of this forthcoming book is to furnish the student beginning analytical chemistry with the facts and theories upon which qualitative and quantitative analysis is based. The treatment has been made as simple as possible. The book gives an adequate introduction to physical chemistry; presents the theories of both complete and partial ionization; and contains a large number of exercises and problems. A conspicuous departure is the use of ionic instead of molecular equations.

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PROBLEMS IN ORGANIC CHEMISTRY

By ERNEST HAMLIN HUNTRESS, Massachusetts Institute of Technology. *International Chemical Series.* 270 pages, $2.25

Intended to supplement the use of a regular textbook in organic chemistry, this new book offers a collection of problems, questions, discussion topics, and review exercises. The first third of the book is devoted to aliphatic compounds, the second third to aromatic compounds, and the remainder to compounds drawn from both groups.

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Hellige Technical Bulletins

A series of technical and descriptive bulletins on the general subject of electrometric pH determinations has recently been prepared in mimeographed form by *Hellige, Inc., 3718 Northern Blvd., Long Island City, N. Y.* The bulletins are primarily concerned with design features and uses for the Hellige pH-Meter and Vacuum-Tube Galvanometer, various types of Glass Electrodes, Reference Electrodes and Their Liquid Junctions, Electrode Supports and Accessory Equipment. A brief paper is also available summarizing the mathematics involved in the Calculation of pH Values from E.M.F. Data.

New Laboratory Colloid Mill

Chemicolloid Laboratories, 44 Whitehall Street, New York City, have developed a new small-scale laboratory model that is ideally suited for both educational and industrial laboratory work. This unit has the same operating principle and rugged construction as the larger models designed for use in industry. A four-page folder, which gives complete details and specifications, is available on request.

New Atomic Weight Chart

A New Atomic Weight Chart, showing the changes announced in the eighth annual report of the Committee on Atomic Weights of the International Union of Chemistry, has just been published by the *Central Scientific Company, Chicago, Ill.* This chart is printed in black on heavy muslin and is provided with common rollers at top and bottom. It is 62″ wide by 42″ high. According to the publisher the large letters and figures are easily read from any location in a classroom of average size.

Foamex

In the manufacture of washable wall paper, the sizes chiefly used today are made from Glue, Casein, or Soya Flour. The printed surfaces are generally hardened with Formaldehyde, Aluminum Acetate, etc. Sizes of this nature develop foaming conditions in their manufacturing processes which interfere with smooth, even printing.

To overcome this foaming, the *Glyco Products Co., Inc.,* has introduced Foamex, a pleasant smelling liquid. When a few drops of Foamex are added to the sized colors or clay or mica in the color pans, foaming is reduced to a minimum and in many cases eliminated completely. Because of the small amount of Foamex required, it is generally introduced by means of an oil-can. Two or three drops of Foamex are all that is necessary as more than that tends to increase surface tension to a greater extent than is desirable.

Further information can be obtained from the manufacturers, *Glyco Products Co., Inc., 148 Lafayette Street, New York City.*

Aristo Catalog

A catalog of Aristo Stop Watches, manufactured in Switzerland for the *Aristo Import Company, 630 Fifth Avenue, New York,* is available to readers of the Journal. The catalog lists both Baumann and Aristo Timers for laboratory and industrial use. It features the new wrist chronographs. A copy of this catalog may be had by writing direct to the company.

Sulfanthrene

A new dyestuff, primarily of interest for printing delustered rayon, has been developed by the *du Pont Company.* Known as "Sulfanthrene" Scarlet 2BN Paste, it is a vat color, somewhat bluer than the Scarlet GN Paste, and is therefore useful where bluer scarlets are desired.

New Silverstat Voltage Regulator for A.C. and D.C. Generators

A simple, moderately priced Silverstat regulator in a range of sizes for the automatic voltage control of small A.C. and D.C. generators is announced by *Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pennsylvania.* There are no vibrating contacts and no parts requiring readjustment or replacement at frequent intervals.

Because small generators are seldom installed where they will receive skilled electrical maintenance, the Silverstat regulator has been designed to be easily placed in operation and to require practically no maintenance. Only simple rheostat adjustments are made when putting it into service, all internal adjustments being made in the factory.

The new regulator is of the direct and quick acting, rheostatic type and regulates the voltage by varying directly the resistance in the field circuit. It is unique in its simplicity of construction and operation, both electrically and mechanically. The regulating action is that of a semistatic device which operates only when a correction in voltage is necessary, which assures long life without necessity for adjustment or replacement of original parts.

The Silverstat consists of a voltage-sensitive stationary coil energized from the machine whose voltage is to be regulated. An iron magnetic circuit, having an air gap, mounts this coil. A moving arm is mounted so that an iron armature on its lower end can move, against the pull of a spring, in the air gap under control of the stationary coil.

The regulating resistance is connected directly in the field circuit (exciter shunt field in A.C. applications and generator shunt field for self-excited D.C. generators).

Since the moving arm is light in weight and has a short travel of only a fraction of an inch, all resistance can be inserted or cut out rapidly or it can vary gradually in fine steps, depending on the change in excitation required. Positive anti-hunting is provided electrically by the use of a damping transformer.

Special effort has been made in designing the Silverstat to eliminate parts requiring maintenance. The few moving parts are permanently supported by leaf type springs thus eliminating friction, wear, and adjustment of such parts. There are no pivots or similar bearings to wear and work loose in service, and require adjustment or replacement. The use of a stationary regulating resistance eliminates the use of lever and linkage systems such as are sometimes employed when a movable resistance assembly is mechanically operated in order to vary its resistance. The damping transformer eliminates the use of dashpots and similar mechanical anti-hunting devices that require maintenance.